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David Edward Broadhead
Iowa State University

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ELECTRICAL DOUBLE LAYER STRUCTURE IN THE PRESENCE OF ADSORBED ORGANIC MOLECULES

by

David Edward Broadhead

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In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

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Dean of Graduate College

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INTRODUCTION

At every interface between two immiscible phases, there exists an array of charged particles and oriented molecules called the electrical double layer. In the case of the metal-solution interface this double layer consists of a layer of electrons (or holes) in the metal, a layer of adsorbed ions and molecules, and a diffuse layer of ions extending out into the bulk solution.

If a potential difference is applied between the metal and the solution, a current may flow across the interface. It is possible, however, that a range of potentials exists for which no charge is transferred across the interface, causing it to act as a capacitor. A system of this second type is called an ideal polarized electrode, and while it can never be fully realized experimentally, close approximations to it are attainable. The study of electrodes which behave as ideal polarized electrodes is known as electrocapillarity.

Historically, mercury has been the metal chosen most frequently in electrocapillary studies. There is a range of about 1.5 volts between potentials respectively at which hydrogen or oxygen evolution reactions lead to appreciable current flows. Since it is a liquid, its surface can be easily cleaned, it is free from mechanical strains, and its interfacial tension is easily measured.

The study of electrocapillarity began with Lippmann

(1) in 1875, who was the first to realize that a measurement of interfacial tension at the mercury-solution interface is meaningless unless the potential difference across the interface is known. Of the early workers, Gouy is the most widely known, due to his extensive cataloging of electrocapillary data for many systems (2-4), and his formulation of a theory of the electrical double layer (5, 6). An excellent review of the earlier work (up to 1947) in electrocapillarity, which is also a good introduction to the subject, was published by Grahame (7).

Since many reviews have been published recently on the subject of the electrical double layer (8-12), no attempt will be made here to summarize the more recent work in this field.

THEORY

The basic thermodynamic relation between the variables at an electrified interface is the Gibbs adsorption equation

$$-d\gamma = QdV + SdT + \sum_i \Gamma_i d\mu_i, \qquad (1)$$

where γ is the interfacial tension, Q is the charge density on the metal surface, V is the polarizing potential, S is the surface entropy, T is the absolute temperature, μ_i is the chemical potential of the ith component of the system, and Γ_i is the surface excess of the ith component. Since two similar equations can be written for the metal and the solution, respectively, it is possible to eliminate two of the terms on the right-hand side of Equation 1. This is usually done by choosing $\Gamma_{Hg} = \Gamma_{H_2O} = 0$.

Since in this thesis we shall be concerned with the adsorption of neutral organic molecules at the interface, the concentration of the electrolyte used and the temperature will always be the same. Hence the Gibbs equation for this special case reduces to

$$-d\gamma = QdV + \Gamma_{org} d\mu_{org} \; . \qquad (2)$$

The interfacial tension now can be seen to be a function of two variables, the potential difference applied across the interface and the chemical potential of the organic substance present in the solution. Experimental data are usually obtained by finding the interfacial tension as a function of potential at constant concentration of the organic solute. A plot of the data obtained in this manner, which is roughly parabolic in shape, is called an electrocapillary curve.

Several useful thermodynamic relations are obtainable from Equation 2. The charge density is found from the first derivative of the electrocapillary curve, since

$$Q = -\left(\frac{\partial \gamma}{\partial V}\right)_{\mu_{org}} . \tag{3}$$

It can be seen from Equation 3 that the maximum interfacial tension occurs when the charge on the mercury is zero. Since the differential capacitance, C, is the derivative of charge with respect to potential,

$$C = -\left(\frac{\partial^2 \gamma}{\partial V^2}\right)_{\mu_{org}} , \tag{4}$$

and the capacity of the electrical double layer can be obtained from the second derivative of the electrocapillary curve.

The surface excess of the organic adsorbate is given by

$$\Gamma_{org} = -\left(\frac{\partial \gamma}{\partial \mu_{org}}\right)_V . \tag{5}$$

It can be seen that if $\Gamma_{org} > 0$, the addition of an organic substance to the solution causes a lowering of the surface tension. Experimentally this lowering is more pronounced near the electrocapillary maximum, i.e., in the region of low charge density. This is because the organic solute, which is usually less polar than the solvent, is displaced from the surface at high charge densities by the water and ionic species present.

In practice it is convenient for calculations to use the surface pressure, π, defined by $\pi = \gamma_o - \gamma$, where γ_o is the interfacial tension obtained with no organic material present in the solution. Equation 5 then becomes

$$\Gamma_{org} = \frac{1}{RT} \left(\frac{\partial \pi}{\partial \ln a}\right)_V , \qquad (6)$$

where a is the activity of the organic solute in the bulk solution. The activity used for the solutes in this thesis is referred to pure liquid solute as standard state and is approximated by the reduced concentration (concentration divided by saturation concentration).

In order to describe the dependence of the amount of organic solute adsorbed on the bulk activity at a given potential, the Frumkin isotherm (13) has been used. The equation for this isotherm is

$$\frac{\theta}{1-\theta} = B_o a \, e^{2\alpha\theta} , \qquad (7)$$

where $\theta = \Gamma/\Gamma_m$ is the fractional surface coverage (Γ_m being the surface excess of the adsorbate at monolayer coverage), B_o is a constant reflecting the interaction of the adsorbate with the mercury surface, and α is a constant reflecting the interactions between molecules of the adsorbate. This equation is based on the regular localized monolayer model, with random distribution of adsorbed molecules in the monolayer.

Two useful standard free energies of adsorption may be obtained from the Frumkin isotherm as follows. Equilibrium between molecules in the solution and on the surface implies

$$\mu_b = \mu_s , \tag{8}$$

where μ_b and μ_s are the chemical potentials of the molecules in the bulk solution and on the surface, respectively. In the solution

$$\mu_b = \mu_b^o + RT \ln a, \tag{9}$$

and on the surface

$$\mu_s = \mu_s^o + RT \ln \gamma_s \frac{\theta}{1-\theta} , \tag{10}$$

where γ_s is the surface activity coefficient.

Substituting Equation 7 into Equation 9 gives

$$\mu_b = \mu_b^o - RT \ln B_o + RT \ln\{e^{-2\alpha\theta}(\frac{\theta}{1-\theta})\} . \tag{11}$$

Therefore, Equation 8, together with Equations 10 and 11 implies that

$$\mu_s^o - \mu_b^o = -RT \ln B_o \tag{12}$$

if

$$\gamma_s = e^{-2\alpha\theta} . \tag{13}$$

The standard state for the adsorbate on the surface implied by Equation 13 satisfies $\lim_{\theta \to 0} \gamma_s = 1$, and physically reflects a state in which an adsorbate molecule has no other adsorbate molecules as near neighbors. Hereafter this will be referred to as an infinite dilution-based standard state. The free energy given by Equation 12 is therefore not very easily interpreted, as it refers to standard states based on pure solute in the solution and infinite dilution on the surface.

The interaction free energy per mole at $\theta = 1$ is given by

$$RT \ln \gamma_a = -2\alpha RT \, . \tag{14}$$

Hence

$$\Delta G_1^o = -RT \ln B_o - 2\alpha RT, \tag{15}$$

where ΔG_1^o is the standard free energy of adsorption referred to standard states based on pure adsorbate both in solution and on the surface.

Similarly, the free energy required to transfer one mole of adsorbate from an infinite dilution-based state in the bulk solution to pure solute is $-RT \ln f_o$, where f_o is the activity coefficient of the adsorbate at an infinite dilution-based state, referred to pure solute as standard state. Therefore

$$\Delta G_o^o = -RT \ln B_o - RT \ln f_o \, , \tag{16}$$

where ΔG_o^o is the standard free energy of adsorption referred to standard states based on infinite dilution of adsorbate both in solution and on the surface.

The free energies given in Equations 15 and 16 have been determined for a number of different adsorbates (14), and a correlation between the free energy of adsorption and the polarizability of the molecule will be established in a later section.

EXPERIMENTAL

Materials

Mercury

Mercury was used as received from Bethlehem Apparatus Co. It was triply distilled under vacuum, and had an evaporation residue of one part in ten million.

Water

All water used in preparing solutions and as the final rinse in the cleaning of glassware was quadruply distilled. Tap distilled water was redistilled from alkaline permanganate solution in a Barnsted still. This water was distilled again through a fused silica continuous double distillation column.

Perchloric acid

Perchloric acid was used as the electrolyte so that results obtained could be more readily compared with those of previous workers in this laboratory. Baker Analyzed Reagent perchloric acid was used without further purification.

The purification of the mercury, water, and perchloric acid was judged to be sufficient by the reproducibility and precision of the electrocapillary curves obtained with no organic adsorbate present. If even a minute amount of a surface active substance had been present in any of these materials, the interfacial tensions would not have remained constant over the time required for a measurement (1 to 5 minutes).

Adsorbates

All organic compounds used were purified by distillation in a Nester/Faust spinning band column. A reflux ratio of 20:2 was maintained during take-off and only the middle one-third of the product was retained. The boiling point of the product was always constant to within 0.3°C. For cyclohexanol and cyclohexanone a vacuum distillation was performed, due to their high boiling points. The pressure in each case was maintained at 70 ± 1 mm of Hg by a pressure regulator, also manufactured by Nester/Faust.

Preparation of solutions

All glassware which came into contact with the solutions or their components was cleaned with alcoholic sodium hydroxide, followed by a solution of potassium dichromate in sulfuric acid, then rinsed several times with tap distilled water and finally with quadruply-distilled water.

The perchloric acid solutions were prepared by first diluting the stock solution to make a large volume of one normal acid, from which the tenth normal solutions were prepared by further dilution. All tenth normal solutions were titrated to the phenolphthalein end point with standard 0.1000N sodium hydroxide. No solution was used which deviated by more than 0.0005N from the desired concentration.

Solutions of 3-pentanol and chloroform were prepared by delivering a measured volume of the liquid with a micropipette into a volumetric flask, and diluting to volume with 0.1N perchloric acid. Cyclohexanol and cyclohexanone solutions were prepared by dilution of the saturated solution with 0.1N perchloric acid.

Solubilities

The solubility of 3-pentanol in 0.1N perchloric acid was determined by preparing several solutions of known concentration, and determining the refractive index and density of these solutions and of the saturated solution. Each of these quantities, when plotted against concentration, yielded a straight line which on extrapolation gave a solubility of 0.588 ± 0.005M.

The solubility of chloroform could not be determined by the above method due to the difficulty of dissolving the chloroform when the solutions were near saturation. Instead, standard solutions were prepared of chloroform in heptane which had been previously saturated with 0.1N perchloric acid. The absorbance of these solutions at 230 Å was measured and plotted against concentration. The chloroform in a saturated (0.1N perchloric acid) solution was then extracted with several known volumes of heptane (previously saturated with 0.1N perchloric acid) and the absorbance of the resulting solution measured. An interpolation of the absorbance plot showed the solubility of chloroform to be 0.0494 ± 0.0005M.

The solubility of cyclohexanol was determined by adding known volumes of 0.1N perchloric acid to a known volume of cyclohexanol until the small bubbles of the organic phase disappeared. Cyclohexanol was then added dropwise until the bubbles remained after vigorous shaking. The average of these results was taken as the solubility, 0.217 ± 0.005M.

The solubility of cyclohexanone was determined from electrocapillary measurements. The technique used will be described in a later section.

Apparatus

The use of the capillary electrometer in obtaining interfacial tension data at the mercury-solution interface began with Lippmann (1) in 1875. All modern electrometers are merely refinements of his basic apparatus. A conical capillary containing mercury is placed in a solution, the interface between the two liquids being formed in the capillary. Methods of varying the pressure at the interface and of applying a potential across the interface must be devised. The interfacial tension, γ, is then determined by

$$\gamma = \frac{R\Delta P}{2\cos\theta} \qquad (17)$$

where R is the radius of the capillary, ΔP the pressure difference across the interface, and θ the contact angle between the mercury and the solution, which is assumed to be zero. If measurements are made with the interface always in the same position, R is a constant. When the interfacial tension is varied by changing the polarizing potential, the pressure ΔP is then adjusted so as to return the interface to its original position.

In order to obtain the radius of the capillary at this reference position, the electrocapillary curve of a standard solution was determined. The maximum interfacial tension of the standard solution being known independently, the radius of the capillary could then be calculated. The solution originally used as a standard was 0.05M sodium sulfate, for which the maximum interfacial tension had been determined by sessile drop measurements (15) as 426.2 ± 0.2 dynes/cm at 25.0 ± 0.3 degrees Centigrade. After several electrocapillary curves of both 0.05M sodium sulfate and 0.1N perchloric acid had been taken with the same capillary, it was decided to use 0.1N perchloric acid as a standard, since the data obtained with this solution were more reproducible. The interfacial tension of 0.1N perchloric acid at the electrocapillary maximum was taken as 425.6 dynes/cm at 25.0 ± 0.1 degrees Centigrade.

The capillary electrometer and its associated pressure system was designed by Gordon Potter and is shown schematically in Figure 1. The capillaries were formed from precision bore Pyrex capillary tubing of internal diameter 0.0008 inches by drawing out the tubing in a gas flame until a tenfold reduction in the outside diameter was attained. The mercury reservoir above the capillary was about 23 cm high, the diameter at the top being much larger in order to minimize the change in height caused by expelling mercury during the experiment.

A tungsten wire was sealed through the glass near the top of the mercury reservoir to provide an electrical connection with the mercury side of the interface. The reference electrode, a Beckman fiber junction saturated calomel electrode, was placed in the solution at the opposite end of the cell from the capillary. A Leeds and Northrup K-3 potentiometer was used to control the potential supplied by four mercury cells. The drift in the potential of these cells after they had been in the circuit for several hours was negligible, so ~~that~~ the potentiometer needed to be calibrated only at 5-10 minute intervals to maintain one millivolt accuracy. Calibration was done with an Eppley standard cell, using a Leeds and Northrup D-C Null Detector, model 9834.

The pressure at the interface was varied by applying pressure to the gas above the mercury with a bellows system. Four 100 cc glass syringes, mounted in a screw-driven press, were used for coarse adjustment, and fine adjustment was achieved with a single 30 cc syringe mounted in a separate press. All syringes were lubricated with stopcock grease to prevent leakage of gas around the edges. A Texas Instruments, Inc. Fused Quartz Precision Pressure Gauge was used to measure the gas pressure, rather than a mercury manometer, as had been previously employed. The use of this instrument was responsible for the greatly improved precision of the electrocapillary data. The precision of the gauge was an order of magnitude greater than the best precision obtained for the electrocapillary data. Since measurements took only a matter of seconds, the interfacial tension could be measured immediately following expulsion of a mercury drop and before a significant amount of impurities could diffuse to the interface.

In order to always return the interface to the same position a Unitron stereomicroscope was used to view the capillary, a high intensity lamp being directed through the length of the cell for illumination. A reticular scale within the eyepiece enabled the position of the interface to be determined with respect to the hole in the tip of the capillary. Optically plane glass was used for the ends of the cell to eliminate distortion.

The height of the mercury column and of the solution above the tip of the capillary were measured with a Gaertner cathetometer to a precision of 0.02 mm. Vibrations were reduced by resting the cathetometer on a concrete block stand and by attaching the capillary electrometer to a Dexangle frame which rested on a heavy piece of soapstone.

Temperature control was achieved by the use of a steam-reheat air conditioner which maintained the temperature of the air surrounding the electrometer and mercury column at 25 ± 1 degree Centigrade. Water from a large bath thermostated to 25.0 ± 0.1 degrees Centigrade by a Haake temperature controller was circulated through coils in the center of the electrometer.

Procedure

As was noted by Kelsh (16), newly prepared capillaries were found to take up to two weeks after initial wetting to obtain a constant radius. All capillaries were therefore aged by soaking in 0.1N perchloric acid solution for at least two weeks before calibration. Since a different capillary was used for each adsorbate studied, it was possible to dismantle and thoroughly clean the electrometer cell before each new set of experiments, thereby removing any traces of the previous adsorbate. After the initial cleaning, the cell was merely rinsed several times with the solution to be added.

After pouring the solution into the cell and installing the calomel electrode, cathetometer readings were taken of the top of the mercury reservoir, the level of the solution in the cell and the bottom of the capillary. These readings were taken only at the beginning and end of each experiment, since the mercury level only dropped by about a tenth of a millimeter during each run.

For the first few electrocapillary curves taken, purified nitrogen was bubbled through the cell prior to the experiment to remove oxygen from the solution. After retaking these curves without first removing the oxygen, it was found that there was no detectable difference in the results, and the procedure was discontinued.

In taking each data point, the potentiometer was first calibrated and the desired potential applied. A drop of mercury was then expelled from the tip of the capillary to provide a fresh surface, presumably free of impurities. The pressure was then adjusted with the bellows to bring the interface to the reference point in the capillary, and the pressure gauge was read. Several oscillations of the interface were made about the reference point by means of the bellows to make sure the mercury was not sticking at this point. Another drop of mercury was expelled and the process repeated as a check. Readings were usually reproducible to within 0.03 dynes/cm.

In order to observe any time-dependent errors in the data, points were taken at even 100 mV intervals proceding from the lowest to the highest potential applied, then the 50 mV points in between were taken in the reverse direction.

Problems

Although interfacial tensions were reproducible to within 0.03 dyne/cm, it was found that the scatter of the points when plotted against potential was more than an order of magnitude larger than this for 3-pentanol. When taking the data it was noticed that the initial value of the interfacial tension was not very reproducible, but if a time varying from three to twenty minutes elapsed after the expulsion of a mercury drop, reproducibility was obtained. At the time the possibility of impurities was not considered, as a gas phase chromatographic analysis had shown that any impurities in the 3-pentanol were less than one-tenth of one percent. On later reflection, however, it was decided that impurities, even in this low a concentration, could have reached the interface in appreciable amounts by ten minutes or so.

When the chloroform data were taken the initial value of the interfacial tension was recorded, assuming that coverage of the surface with chloroform would be as complete as possible within a few seconds due to its relatively high concentration compared to that of any impurities present. Considerable scatter was still obtained in the electrocapillary points for chloroform, but this time the scatter appeared to be time-dependent. In order that the reference port of the pressure gauge be at the same pressure as the gas above the solution, the central port of the electrometer cell had been left loosely stoppered. Enough chloroform had evidently evaporated from the solution to cause a measurable rise in the interfacial tension during the experiment.

A method of correcting the data for evaporation was devised, and will be presented in a later section. To prevent this from being as much of a problem, however, relatively non-volatile solutes were chosen for future work. Much less scatter was observed in the electrocapillary curves for cyclohexanol.

After much deliberation, an absurdly simple solution to the evaporation problem was devised. The reference port of the pressure gauge was simply connected to the central port of the electrometer cell, thus providing a closed system and minimizing evaporation. The data for cyclohexanone were taken using this modified apparatus, and the scatter in the data was greatly reduced.

When solutions of the three lower concentrations of cyclohexanone were run, reproducible initial values for the interfacial tension were not obtainable for potentials negative with respect to the electrocapillary maximum. A gas chromatogram was taken of the cyclohexanone used, and no impurity could be found with a concentration greater than one-tenth of one percent. Due to the method used in analyzing the data, however, useful results were still obtained for this compound.

ANALYSIS OF RESULTS

Computer Programs

Several computer programs were written for use in data analysis. The output from these programs could probably have been obtained more quickly by hand calculation and graphing, since much time was spent in devising, coding, debugging, and revising the programs. Hand calculations, however, are subject to error and hand plotting to bias. And while the saving in real time may have been negative, the saving in boredom was highly positive.

Although the use of the programs will be described in the next section, a few features common to all of them are given here. All programs were written in the Full Fortran IV language, compiled in Fortran G, and run on an IBM 360/65 computer. A listing of three of the programs (EC1, EC2, and EC5) may be found in Appendix B. The other two programs used are not given, since they merely involve reading in data to be graphed by the plotter. The subroutines PCLA (replace one polynomial by another), PDER (derivative of a polynomial), POLRT (roots of a polynomial), and PVAL (value of a polynomial) are not listed, as they are part of the IBM Scientific Subroutine Package (17). GRAPH, LETTER, and ORIGIN are part of a resident plotting routine SIMPLOTTER (18), and OPLSPA (19) is a resident curve fitting subroutine which calculates least squares polynomial coefficients by an orthogonal polynomial method.

Method of Analysis

A general description of the method used to analyze the data will be given in this section. Complications obtained with individual adsorbates and the method of handling them will be discussed in the next section.

The first computer program used, EC1, converts the pressure readings to interfacial tension and fits the resulting electrocapillary data with an analytical expression. The expression chosen as the best fit to the data in each case was the least squares polynomial of highest degree (less than or equal to degree ten) which had no point of inflection in the region of the data[1]. A complete description of EC1 may be found in the listing of the program itself in Appendix B. An example of part of the output from the program is given in Appendix C and Figures 2-5.

When all the electrocapillary curves for a particular adsorbate had been analyzed by EC1, the polynomials fit to each curve were input to the second program, EC2. This program was used to shift the reference point of the potential

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[1] A portion of the electrocapillary curve with positive curvature would imply a negative differential capacity in that region, a physically untenable result.

scale from the saturated calomel electrode potential to that of the electrocapillary maximum of the base electrolyte. In addition the family of electrocapillary curves for the given adsorbate was plotted and the dependence of surface pressure, π (calculated from the least squares polynomials), on potential and ln activity was established. A listing of EC2 may be found in Appendix B.

For each potential (usually 50 millivolt intervals were chosen) a plot was made by the third program, EC3, of the surface pressure vs. ln activity points. These plots were found to be superimposable (within experimental error) by shifting the entire graph horizontally along the ln a axis. One of the π-ln a curves, usually for a potential near the electrocapillary maximum, was chosen as a reference and the magnitude of the shift required for superposition, LNAINC, was found by eye and recorded as a function of potential.

The data thus obtained were read into the fourth program, EC4, which plotted all of the shifted π-ln a points on a single composite curve. An internal smoothing routine in SIMPLOTTER was used to plot a smooth curve through these points on a separate graph.

An interesting application of the superimposability of the surface pressure curves is a new method for determining solubility. A solution of known concentration is prepared and an electrocapillary curve of the solution taken. For each potential a value of the surface pressure, π, is calculated, and the ln a corresponding to this π is read from the composite π-ln a curve. When the shift for the given potential, LNAINC, is added to this ln a, the actual ln a of the solution is recovered. The activities obtained are averaged over a number of potentials, and the solubility, c_o, can then be calculated, since both c and $a = c/c_o$ are known. This method was used to determine the solubility of cyclohexanone.

In order to obtain the surface excess, Γ, the derivative of the composite π-ln a curve must be obtained. This may be done by graphical differentiation or by fitting the curve with a theoretical expression and differentiating analytically. Since the second method is more aesthetically pleasing, the surface pressure curve was tested against several different equations. The best fit to the data, however, was provided indirectly by the Frumkin isotherm, for which an analytical relation between π and ln a is impossible to obtain. In order to use a Frumkin isotherm, therefore, it was necessary to differentiate graphically the composite π-ln a curve to obtain Γ.

The computer-smoothed curve output from EC4 was found to contain several irregularities in slope, and was therefore resmoothed with French curves. Tangents to this curve were constructed, and two points were read from opposite ends of each tangent. These points, along with the coordinates of the point on the curve to which the tangent was drawn, were used as part of the input data for the last computer program, EC5.

EC5 was written as a three-part program. The first section reads in actual data points from the linear portion of the composite π-ln a curve, which are then used to calculate the maximum surface excess, Γ_m (the surface excess corresponding to monolayer coverage). Next the points obtained in the graphical differentiation are read and converted first to surface excess, Γ, and then to fractional surface coverage, θ. The array of ln a vs. θ points thus obtained is then fit with a Frumkin equation. The last part of the program reads in an array of potential vs. LNAINC points and these, together with the parameters of the Frumkin equation, are used to calculate the free energies of adsorption, ΔG_0^o and ΔG_1^o, as functions of potential.

Accuracy of Electrocapillary Curves

As was discussed in the experimental section, good precision was not obtained in the electrocapillary curves for several compounds because of the presence of impurities and loss of solute by evaporation. While nothing can be done ex post facto to regain the precision lost due to impurities, a semi-empirical method was developed to correct the data for evaporation losses. If it is assumed that the concentration decays exponentially with time, as would be true for diffusional flow of vapor away from the surface for a simplified but nonetheless reasonable model, then

$$a = a_0 e^{-\alpha t} , \tag{18}$$

where a_0 and a are the bulk activities of the adsorbate at time 0 and t respectively, and α is the rate constant for the diffusion. The rate of change of interfacial tension, γ,

$$\begin{aligned} \frac{\partial \gamma}{\partial t} &= \left(\frac{\partial \gamma}{\partial \ln a}\right)\left(\frac{\partial \ln a}{\partial t}\right) \\ &= (-\Gamma_m RT\ \theta)(-\alpha) \\ &= A\theta \end{aligned} \tag{19}$$

where $A = \alpha \Gamma_m RT$.

The fractional surface coverages, θ, were estimated by plotting preliminary π-ln a curves, forming a preliminary composite curve, and graphically differentiating. The constant A was estimated by plotting separate electrocapillary curves for the 100 mV and 50 mV interval points, and finding the difference, $\Delta\gamma$, between these curves at some potential. The time difference between the points on each curve was either known or estimated. The correction was then calculated for each data point and the data were corrected before submitting it to the program EC1.

The corrections applied, while small (see Table 1, Appendix D), greatly improved the precision of the electrocapillary data for chloroform and cyclohexanol. They were not applied to 3-pentanol, as the scatter due to impurities was too large to enable the constant A to be determined.

Another source of error was in the measurement of the height of the mercury column with the cathetometer. While the difference between individual readings was generally only a few hundredths of a millimeter, the heights of the mercury column measured on different days (even without expelling any mercury between measurements) sometimes differed by as much as a tenth of a millimeter, which would introduce an error of 0.05 dyne/cm in the interfacial tension. To minimize this error, a plot of mercury height vs. number of drops expelled from the capillary was made, and a straight line was drawn through the points. This straight line was then used to find both the mercury height at the start of each experiment, and the correction which was applied by EC1 to each data point for loss of mercury during the experiment.

Some error is undoubtedly introduced by attempting to fit the electrocapillary curve with a finite polynomial rather than an infinite series. An examination of the graphs produced by EC1, however, reveals that this error is within the scatter of the points in all cases. This means that the root mean square deviation of the data points from the polynomial fit to these points provides a good measure of the precision of the data. Table 1 lists the RMS deviation, along with other information on the precision of the various electrocapillary curves.

The fit in some cases is so good that the capacity curves produced by double differentiation of the electrocapillary curve reproduce not only the shape of the capacity curves obtained by direct measurement, but also are close to being numerically correct. Figure 5 compares the capacity curve for pure 0.1 N $HClO_4$ obtained from electrocapillary measurements with that obtained directly, and the fit is seen to be remarkably good except near the ends of the curve, where the electrocapillary data are not sufficient to permit an accurate determination of the curvature.

Accuracy of Results

While the errors in the taking and fitting of the original data are naturally propagated to the final results, there are other errors which arise in the course of analyzing the data due to the imperfect methods used.

In the process of superimposing the π-ln a curves, which was done by eye, it was assumed that surface pressures near the electrocapillary maximum potential were the most accurate,[1] and the curves were shifted to superimpose in this region. It is believed that this assumption is justified by the

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[1] Any error caused by a mistake in the radius of the capillary would be smallest near the electrocapillary maximum potential of the base electrolyte since the calibration point was the electrocapillary maximum.

larger scatter in the points of the composite curves in the low π region. Possibly the curves could have been superimposed with less scatter in all regions had this assumption not been made, but no unbiased way was found to do this. At high positive or negative potentials the surface pressures were too low to obtain an accurate measure of the shift required for superposition. This was made difficult both because of the increased scatter in the low π region and the low slope of the curve.

Before drawing a smooth curve for the composite π-ln a data certain points were deleted. Points at high positive or negative potentials were omitted for 3-pentanol and cyclohexanol, as explained above. While only the 100 mV interval points are shown in Figures 10 and 12 for clarity, the 50 mV interval points were included when drawing the curve. For chloroform and cyclohexanone, larger regions were omitted due to the bad scatter of the points caused by impurities. In the case of chloroform the impurity was adsorbed mainly on the positive side of the electrocapillary maximum, while for cyclohexanone it was adsorbed on the negative side.

Possibly the largest sources of error in the analysis of the data were the inaccuracies inherent in drawing a smooth curve through the π-ln a points and in drawing tangents to this curve. Some of the bias in drawing the curve was eliminated by using the computer smoothing routine, but the graphical differentiation still caused considerable scatter in the surface excesses obtained (see Figures 14-17). Although this scatter is large, the Frumkin isotherm which was fit to the data, when used to calculate theoretical π-ln a points, fit the original π-ln a points extremely well (see Figures 10-13).

Special problems arose in the analysis of the chloroform data due to its high volatility and low surface activity. When the π-ln a points were originally plotted it was discovered that they were all superimposable except the points for the saturated solution, which were superimposable on a different curve, parallel to the first but at higher surface pressure. Evidently considerable chloroform in the unsaturated solutions had evaporated during the process of preparing and mixing them, while any chloroform evaporating from the saturated solution during this process was replaced from the chloroform phase. Since the solutions had been prepared the day before the electrocapillary data were taken, and had been stirred overnight, considerable evaporation could have occurred around the stopper of the flask during this time. In fact it was later found that if a flask containing a saturated solution with a small lens of chloroform on the bottom was left standing for a few days, the lens would disappear.

Since the π-ln a points for the lower concentrations were superimposable it was assumed, as for the previous evaporation correction, that the concentration decayed exponentially with time. Since the time of evaporation was approximately the same for each solution, the π-ln a points were shifted by the same amount to a lower ln a. The composite curve thus obtained, while not as accurate due to the approximate method of correction, has a scatter comparable to that found for the other adsorbates studied.

Due to the low surface activity of chloroform, monolayer coverage was not approached even with a saturated solution. A special technique was therefore used to approximate the maximum surface excess. It was assumed that the data could be fit by a Frumkin isotherm, for which a plot of ln a vs. θ is symmetric on inversion through the point ($\theta = \frac{1}{2}$, ln a = ln $a_{\frac{1}{2}}$). A plot of the surface excess, Γ, vs. ln a was made, and the point of symmetry was determined by eye. Twice the value of Γ at this point was taken as the maximum surface excess.

Results

Electrocapillary curves for the adsorbates studied are given in Figures 6-9. 3-pentanol, cyclohexanol, and cyclohexanone can be seen to shift the potential of the electrocapillary maximum to the right, indicating a preferential adsorption on a negatively charged surface. Chloroform, within experimental error, does not shift the potential of the electrocapillary maximum at all.

Coefficients of the polynomials fit to each electrocapillary curve were listed as part of the output data of program EC2. These are given in Appendix C, along with the coefficients of the polynomials after transformation to the new potential scale (volts vs. electrocapillary maximum). A table of interfacial tensions calculated from these polynomials is also given for each adsorbate.

The composite π-ln a points and the curve calculated from the Frumkin equation can be seen in Figures 10-13.

The output of program EC5 for each adsorbate (see Appendix C) lists the Frumkin parameters obtained, and a table of interfacial variables experimentally determined and those calculated from the Frumkin equation.[1]

Rather than draw individual adsorption isotherms for each potential, it was found that if the dimensionless variables θ, fractional surface coverage, and $a/a_{\frac{1}{2}}$, reduced activity[2], were used, a single isotherm was sufficient to describe the data at all potentials (see Figure 18). In fact, superimposability of the surface pressure plots is a sufficient condition for the existence of a single dimensionless isotherm. Superimposability implies that

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[1] The calculated values of π are not necessarily close to the experimental values, since they correspond to different activities.

[2] $a_{\frac{1}{2}}$ is the activity of the adsorbate in the bulk solution at one-half the maximum coverage.

$$\pi = f[\ln a + g(V)] \tag{20}$$

and that the fractional surface coverage is a function of π alone, independent of V, i.e. $\theta = h(\pi)$. Thus

$$\begin{aligned} \ln a &= f^{-1}(\pi)-g(V) \\ &= f^{-1}[h^{-1}(\theta)] - g(V), \end{aligned} \tag{21}$$

or a is the product of two functions, one dependent on θ alone, the other on V alone, and hence $a/a_{\frac{1}{2}}$ will be independent of V.

This can be readily seen in the special case of the Frumkin isotherm, if Equation 7 is written in the form

$$\frac{\theta}{1-\theta} = B_o' \left(\frac{a}{a_{\frac{1}{2}}}\right)e^{2\alpha\theta} \ . \tag{22}$$

$a_{\frac{1}{2}}$ is the only parameter which depends on the potential.

The standard free energies of adsorption ΔF_0^o and ΔF_1^o are plotted as a function of potential in Figures 21 and 22. These were calculated using Equations 16 and 15, where the B_o for each potential was found from the relation

$$\begin{aligned} \ln B_o &= \ln B_o' - \ln a_{\frac{1}{2}} \\ &= \ln B_o' - \ln a_{\frac{1}{2}}' - \text{LNAINC} \end{aligned} \tag{23}$$

where $\ln a_{\frac{1}{2}}'$ is $\ln a_{\frac{1}{2}}$ for the reference potential of the composite surface pressure curve.

INTERPRETATION OF RESULTS

The fact that the π-ln a curves for the adsorbates studied can be superimposed means that the interactions between molecules of the adsorbate (as measured by the constant α of the Frumkin equation) are independent of potential. Only adsorbate-metal interactions (as measured by B_0 or the standard free energies of adsorption) are potential dependent. This is physically reasonable, as changing the electrical state of the interface would not be expected to have an appreciable effect on intermolecular forces. Parsons has observed superimposability[1] for a number of other compounds: thiourea (20, 21), sodium benzene m-disulfonate (22), n-butanol (23), and acetanilide (24).

The only compound known to this author for which the π-ln a curves are not superimposable[2] is phenol (16, 25). It is now believed (26) that there is an interaction between the electrode and the π-electrons of the benzene ring which causes the molecule to lie parallel to the surface when the mercury is positively charged. When the mercury is

---

[1] Although Parsons has chosen the charge, rather than the potential as his electrical variable, he has shown (23) that within experimental error superimposability of the π-ln a curves is also possible if the potential is chosen.

[2] This does not mean to imply that other such compounds have not been observed, only that few authors have attempted superimposability.

negatively charged, the molecules undergo a gradual reorientation to a position perpendicular to the surface. This reorientation alters the molecular area at full coverage (and hence Γ_m), as well as the intermolecular forces. Although a Frumkin isotherm could be fit to the data for such a compound, the three parameters B_o, α, and Γ_m would all vary with potential, and consequently would not be as easily interpretable.

It appears that unless some phenomenon such as reorientation occurs to change the intermolecular forces, these interactions should be independent of potential. Compounds for which molecular interactions are independent of the electrical state of the interface will henceforth be termed I-compounds, for brevity.

Previous work in this laboratory (14,16,25,27) has been analyzed by means of a generalized Frumkin isotherm

$$\frac{\theta}{1-\theta} = B_o' \, a \, e^{2\alpha\theta} \, e^{-(S\Phi/RT)} , \tag{24}$$

where S is the molar area of the adsorbate at full coverage,

$$\Phi = \int_0^V \left(\frac{\partial Q}{\partial \theta}\right)_V dV ,$$

and the other parameters are as previously defined. Comparison of Equations 22 and 24 shows that

$$\Phi = \frac{RT}{S} \ln a_{\frac{1}{2}} . \tag{25}$$

For I-compounds, Φ has been shown to be a function of V alone (independent of Γ), and hence the surface charge density, Q, varies linearly with Γ (at fixed V), as was shown in Reference 25. Thus a linear variation of charge density with coverage appears to be justified for I-compounds. This is the basic assumption initially propounded by Frumkin (13), and used in this laboratory to obtain adsorption information from double layer capacitance measurements.

A comparison of the standard free energies of adsorption, ΔG_0^0 and ΔG_1^0, obtained for the various adsorbates studied should give an indication of the types of forces responsible for the adsorption. A model based on van der Waals forces which appears to represent the data fairly well has been published by Steele and Halsey (28). It is derived on the assumption of hard-sphere monolayer adsorption and applied to the adsorption of rare gas atoms on a solid surface. The formula which they obtain for the energy of interaction of an atom with the surface, ϵ^*, is

$$\epsilon^* = \frac{N_0 mc^2 \pi}{D^3} \left[\frac{\alpha_1 \alpha_2}{\frac{\alpha_1}{\chi_1} + \frac{\alpha_2}{\chi_2}}\right] , \qquad (26)$$

where N_0 is the number of adsorbent particles per cubic centimeter, m is the mass of the electron, c is the velocity of light, D is the distance of closest approach of adsorbate and adsorbent molecules, and α and χ are the polarizabilities and diamagnetic susceptibilities, respectively, of the adsorbate and adsorbent molecules.

In applying this formulation to the mercury-solution interface we now have an adsorbent, Hg, and two adsorbates, water, w, and an organic substance, i. Thus

$$\epsilon_w = \frac{N_o m c^2 \pi}{D_w^3} \left[\frac{\alpha_{Hg} \alpha_w}{\frac{\alpha_{Hg}}{\chi_{Hg}} + \frac{\alpha_w}{\chi_w}} \right] \tag{27}$$

and

$$\epsilon_i = \frac{N_o m c^2 \pi}{D_i^3} \left[\frac{\alpha_{Hg} \alpha_i}{\frac{\alpha_{Hg}}{\chi_{Hg}} + \frac{\alpha_i}{\chi_i}} \right] \tag{28}$$

Now the change in interaction energy when one mole of organic solute replaces an equal area of water molecules is given by

$$\Delta E_i = -N\epsilon_i + N\epsilon_w \left(\frac{\bar{V}_i^{2/3}}{\bar{V}_w^{2/3}} \right) , \tag{29}$$

where N is Avogadro's number, and $\bar{V}_i$ and $\bar{V}_w$ are the molar volumes of the organic substance and of water, respectively. It is assumed that since the model applies to hard-sphere adsorption, the ratio of the areas covered by the molecules is the same as the ratio of their molar volumes to the two-thirds power.

Substituting Equations 27 and 28, dividing by $\bar{V}_i^{2/3}$, and assuming that the entropy term is negligible gives

$$-\frac{\Delta G_i}{\bar{V}_i^{2/3}} = \frac{k\alpha_{Hg}}{L_i} \left[\frac{\alpha_i}{\bar{V}_i^{2/3}} - \left(\frac{L_i}{L_w} \right) \frac{\alpha_w}{\bar{V}_w^{2/3}} \right] , \tag{30}$$

where $k = NN_o mc^2\pi$, $L_i = D_i^3 \left(\frac{\alpha_{Hg}}{\chi_{Hg}} + \frac{\alpha_i}{\chi_i}\right)$, and $L_w = D_w^3\left(\frac{\alpha_{Hg}}{\chi_{Hg}} + \frac{\alpha_w}{\chi_w}\right)$. The solutes investigated in this study were all organic molecules and all were found to adsorb with orientation parallel to the surface. In this circumstance their structures were such that D_i should be nearly the same for all solutes. For these same solutes the ratio $\frac{\alpha}{\chi}$ varied from -33×10^6 to -44×10^6 c.g.s. units, and the ratio for mercury was about -30×10^6 c.g.s. units. Hence L_i should be constant for these solutes within a range $\pm$ 10%. If L_i is considered constant a plot of $-\frac{\Delta G_i}{\bar{V}_i^{2/3}}$ vs. $\frac{\alpha_i}{\bar{V}_i^{2/3}}$ should yield a straight line.

Such plots are given in Figures 21 and 22 for ΔG_o^o and ΔG_1^o at the potential of the electrocapillary maximum for the inert electrolyte. Points obtained for the four adsorbates studied are given, as well as points obtained for other adsorbates by previous workers in this laboratory through measurement of differential capacitance (14). The point for phenol on both graphs is clearly not on the line, which is to be expected since it was obtained by a method which assumed that it was an I-compound and it is not. While the model used is of course not strictly applicable to the mercury-solution system, the linearity of the plots suggests that van der Waals forces are of prime importance in adsorption at the mercury-solution interface.

The surface area occupied by a molecule of the adsorbate at full monolayer coverage may be obtained by taking the reciprocal of Γ_m. Experimental surface areas are compared with those derived from molecular models in Table 2. Godfrey space-filling molecular models were arranged on a flat surface and photographed from directly above. Areas were then calculated assuming that the molecules were allowed to rotate about their geometric centers, and that they were arranged in a hexagonal array covering the surface.

Experimental surface areas can be seen in all cases to be somewhat larger than those obtained from the models, which is to be expected since the molecules are probably not localized in a regular array on the surface even at full coverage. The experimental areas of the larger molecules indicate that they are arranged parallel to the surface, rather than perpendicular. The hydroxyl group of cyclohexanol is most likely oriented in an equatorial position with respect to the ring. An anomaly in the case of cyclohexanone has yet to be explained.

Of the two main techniques used to obtain information on adsorption at the mercury-solution interface-interfacial tension and differential capacitance measurements-there has been considerable controversy in the literature (29-31) as to which is the more accurate. Most authors have compared the two methods by looking at the interfacial tension obtained directly from electrocapillary curves, γ_m, and that obtained indirectly by double integration of capacity curves, γ_c. Deviations between γ_m and γ_c are generally on the order of

0.5 dynes/cm, which is about the same as the experimental error of the measurements. Considering the greatly improved precision now obtainable in the measurement of γ_m, direct measurement would seem to be the preferable technique.

The use of a model based on the linear variation of Q with Γ at constant V (14, 16, 25, 27) to infer adsorption from differential capacitance measurements has been justified for I-compounds. If capacitance data is used this technique would seem to be preferable to that of doubly integrating the capacitance data, since it would presumably involve less multiplication of errors.

SUMMARY

The adsorption of chloroform, 3-pentanol, cyclohexanol, and cyclohexanone at the mercury-0.1N perchloric acid solution interface has been studied. Interfacial tension measurements were made with a capillary electrometer of greatly improved precision.

In the analysis of the electrocapillary data obtained for each adsorbate it was discovered that the surface pressure - ln activity curves for different potentials could be superimposed by a translation along the ln a axis. Implications of this superimposability are (1) that the interactions between molecules of the adsorbate are independent of the electrical state of the interface and (2) that the surface charge density varies linearly with surface excess (at fixed potential).

The Frumkin isotherm was used to fit the data for each adsorbate, and two standard free energies of adsorption were calculated from its parameters, one referring to standard states based on infinite dilution both in solution and on the surface and the other referring to standard states based on pure adsorbate both in solution and on the surface. A correlation between these standard free energies of adsorption and polarizabilities of the molecules was established, indicating that van der Waals forces are primarily responsible for the adsorbate-adsorbent

interactions.

Molecular areas determined experimentally were found to compare favorably with those obtained from molecular models.

The high precision of the interfacial tension measurements obtained would seem to favor direct measurement, rather than inference from capacitance measurements, as the more accurate method of obtaining adsorption parameters.

SUGGESTED MODIFICATIONS AND EXTENSIONS

Several experimental modifications should be made to increase both the accuracy and precision of the data. In order to study compounds of high volatility, an apparatus should be constructed to prepare the solutions from the saturated solution directly in the cell, to avoid loss of solute by evaporation during the mixing and transferring of the solution. Kaganovich, Gerovich, and Gusakova (32) have recently designed and used such an apparatus to find the electrocapillary curves of several volatile adsorbates.

Since even minute amounts of a surface active impurity can affect the accuracy of the electrocapillary data, the impurities remaining after distillation should be removed by a gas chromatographic separation.

It would be instructive to retake a family of electrocapillary curves for one of the adsorbates already studied and note any difference in the results obtained after these two modifications. If these modifications cause a significant improvement in the accuracy of the data, a critical comparison should be made between analyses of the data using potential and using charge as the electrical variable.
It is possible that improved precision could enable a decision to be made in this continuing controversy (10, 23, 24, 33-37).

With data of improved accuracy it would be interesting to see if fitting the electrocapillary curves in sections, rather than as a whole, would cause a better correspondence between capacitance curves obtained directly and those obtained by double differentiation of electrocapillary curves. A computer program to fit the electrocapillary curve in sections has been recently written by Mohilner (38).

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Special thanks must also go to Gordon Potter, who designed most of the experimental apparatus used.

APPENDIX A

Figures Cited in Text

The numerical data corresponding to the graphs of Figures 2 - 18 may be found in Appendix C.

Figure 1	Diagram of apparatus
Figures 2-5	Example of output from computer program EC1
Figures 6-9	Electrocapillary curves
Figures 10-13	Composite π-ln a curves
Figures 14-17	ln a vs. θ curves
Figure 18	Adsorption isotherms
Figures 19-20	Free energy vs. potential curves
Figures 21-22	Correlation of free energy with polarizability

Figure 1. Diagram of apparatus. Four mercury cells are used to supply a potential to the potentiometer, which applies a known potential between the mercury in the capillary and the saturated calomel electrode used as a reference. Pressure is applied to the gas above the mercury by a set of screw-driven glass syringes, and is measured with the fused quartz precision pressure gauge. The capillary is viewed through a binocular microscope (not shown) set in front of the cell.

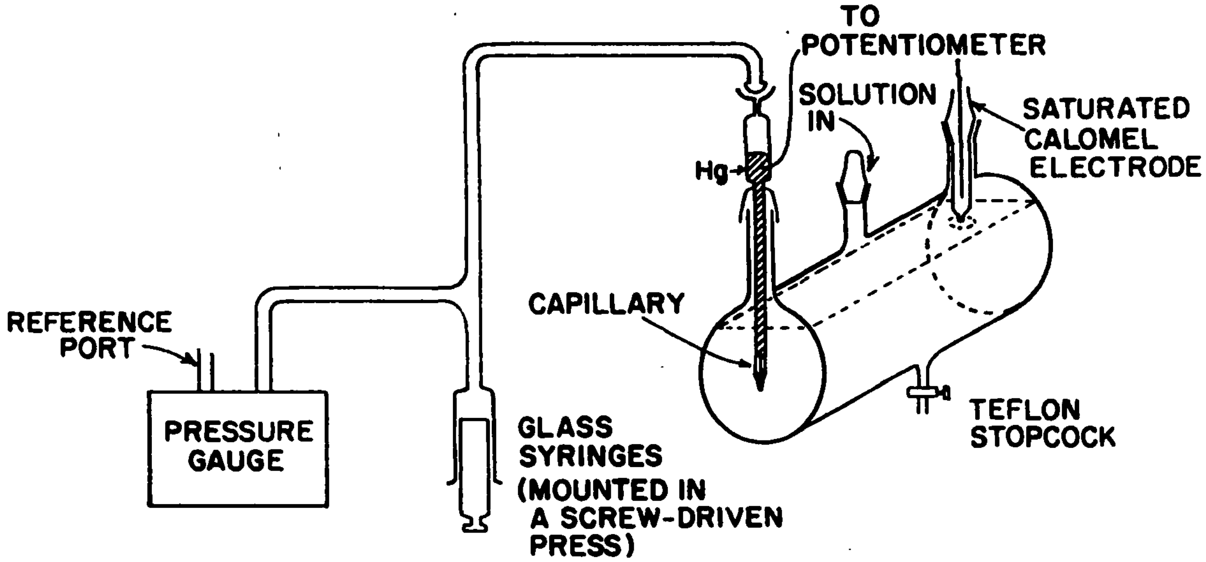

TO
POTENTIOMETER
SOLUTION
IN
SATURATED
CALOMEL
ELECTRODE
Hg
CAPILLARY
REFERENCE
PORT
PRESSURE
GAUGE
GLASS
SYRINGES
(MOUNTED IN
A SCREW-DRIVEN
PRESS)
TEFLON
STOPCOCK

Figure 2. Example of an electrocapillary curve output from computer program EC1. The solution used was 0.100 N $HClO_4$ with no organic adsorbate present. Points shown are experimental data. The curve is the least squares polynomial fit to the data.

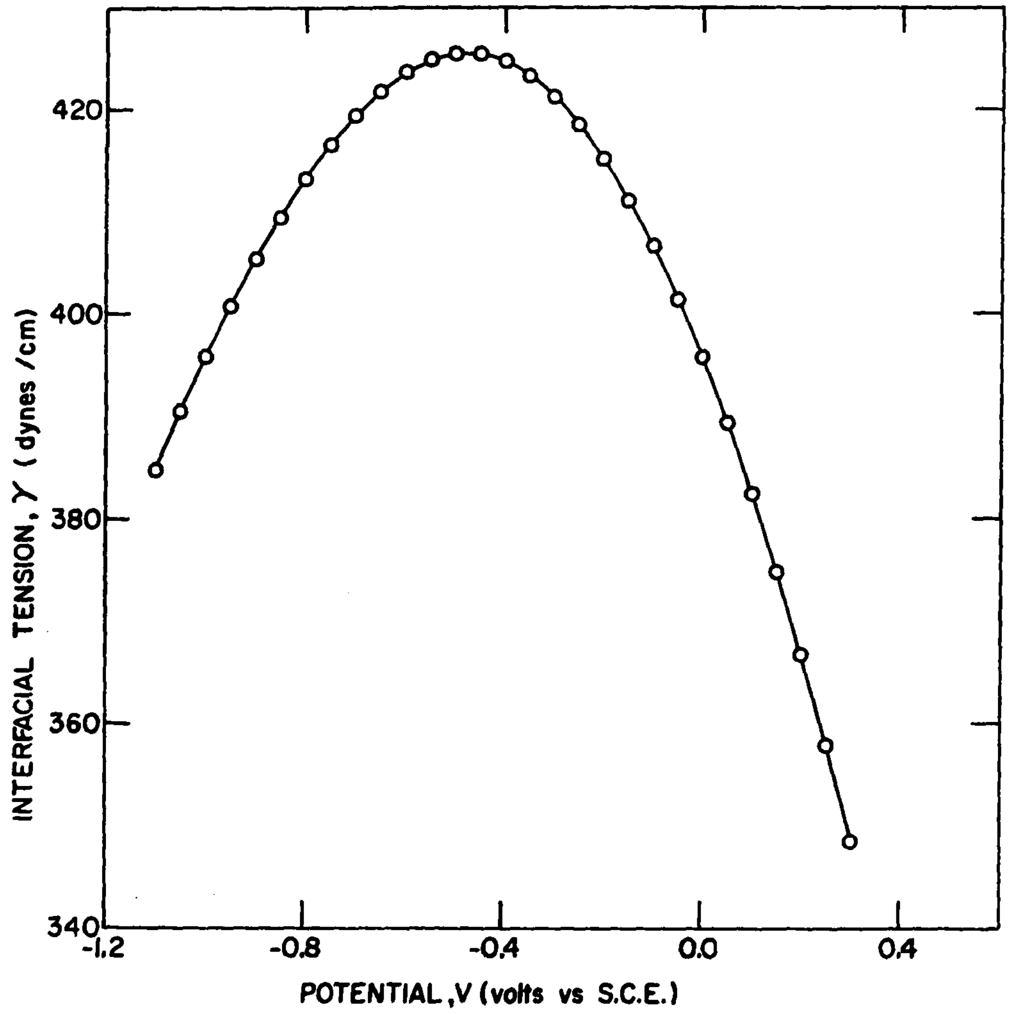

INTERFACIAL TENSION, γ (dynes /cm)
340
360
380
400
420
-1.2
-0.8
-0.4
0.0
0.4
POTENTIAL,V (volts vs S.C.E.)

Figure 3. The region of the electrocapillary curve of Figure 2 near the electrocapillary maximum, shown on an expanded scale.

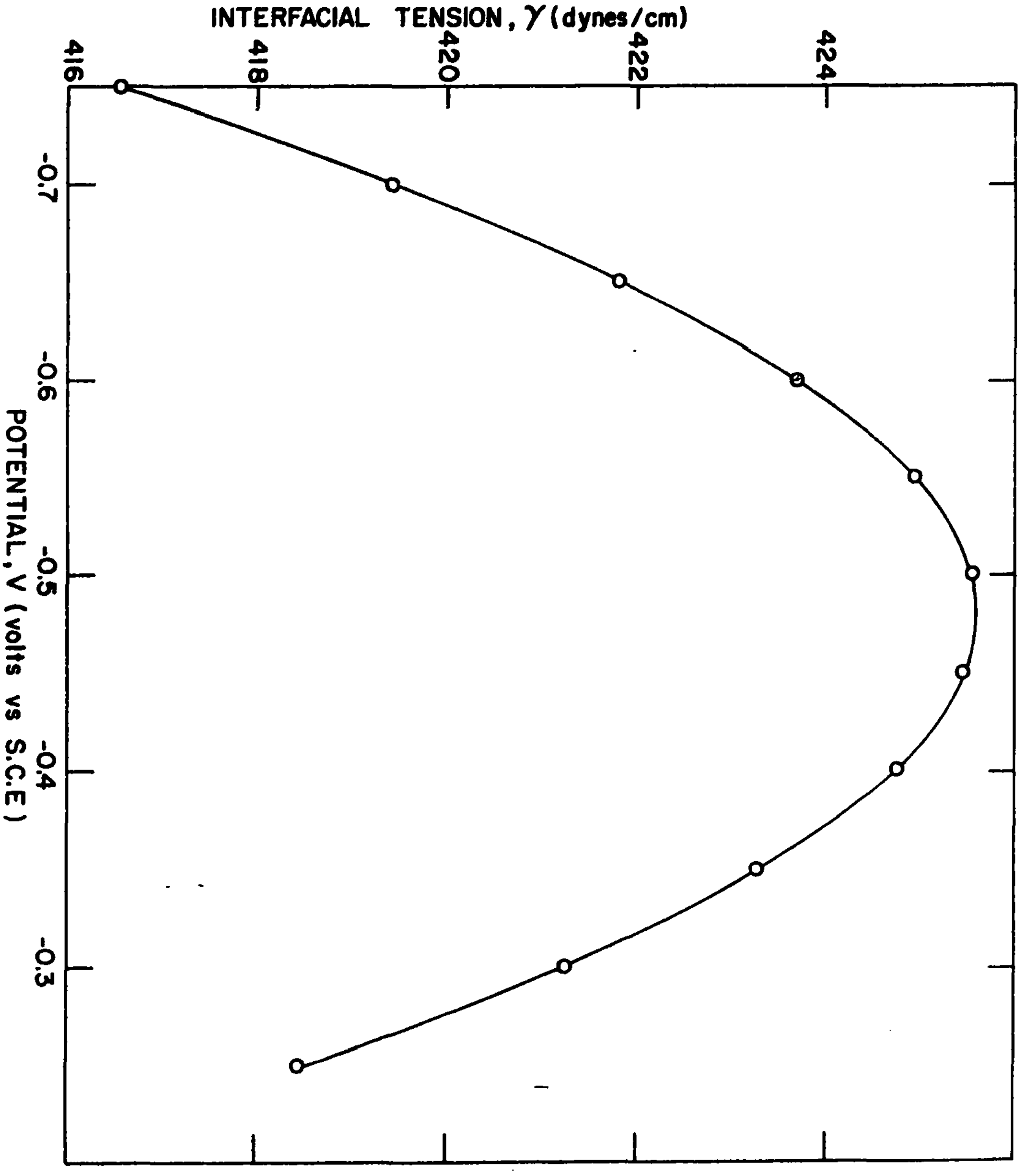

INTERFACIAL TENSION, γ (dynes/cm)
416
418
420
422
424
-0.7
-0.6
-0.5
-0.4
-0.3
POTENTIAL, V (volts vs S.C.E)

Figure 4. Surface charge per unit area on the mercury side of the double layer. The curve is calculated from the least squares polynomial fit to the electrocapillary data of Figure 2.

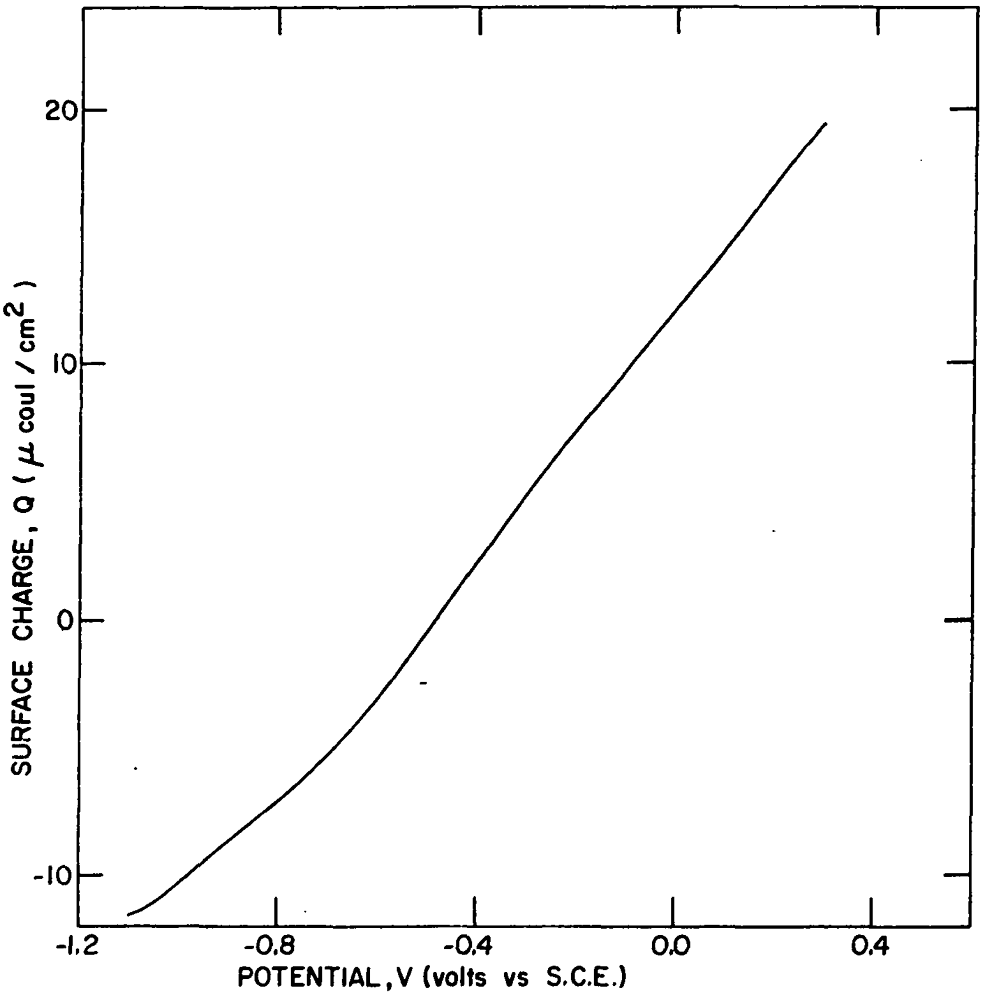

SURFACE CHARGE, Q (μ coul / cm^2)
20
10
0
-10
-1.2
-0.8
-0.4
0.0
0.4
POTENTIAL, V (volts vs S.C.E.)

Figure 5. Differential capacitance per unit area of the double layer. Points shown are direct experimental data. The curve is calculated from the least squares polynomial fit to the electrocapillary data of Figure 2.

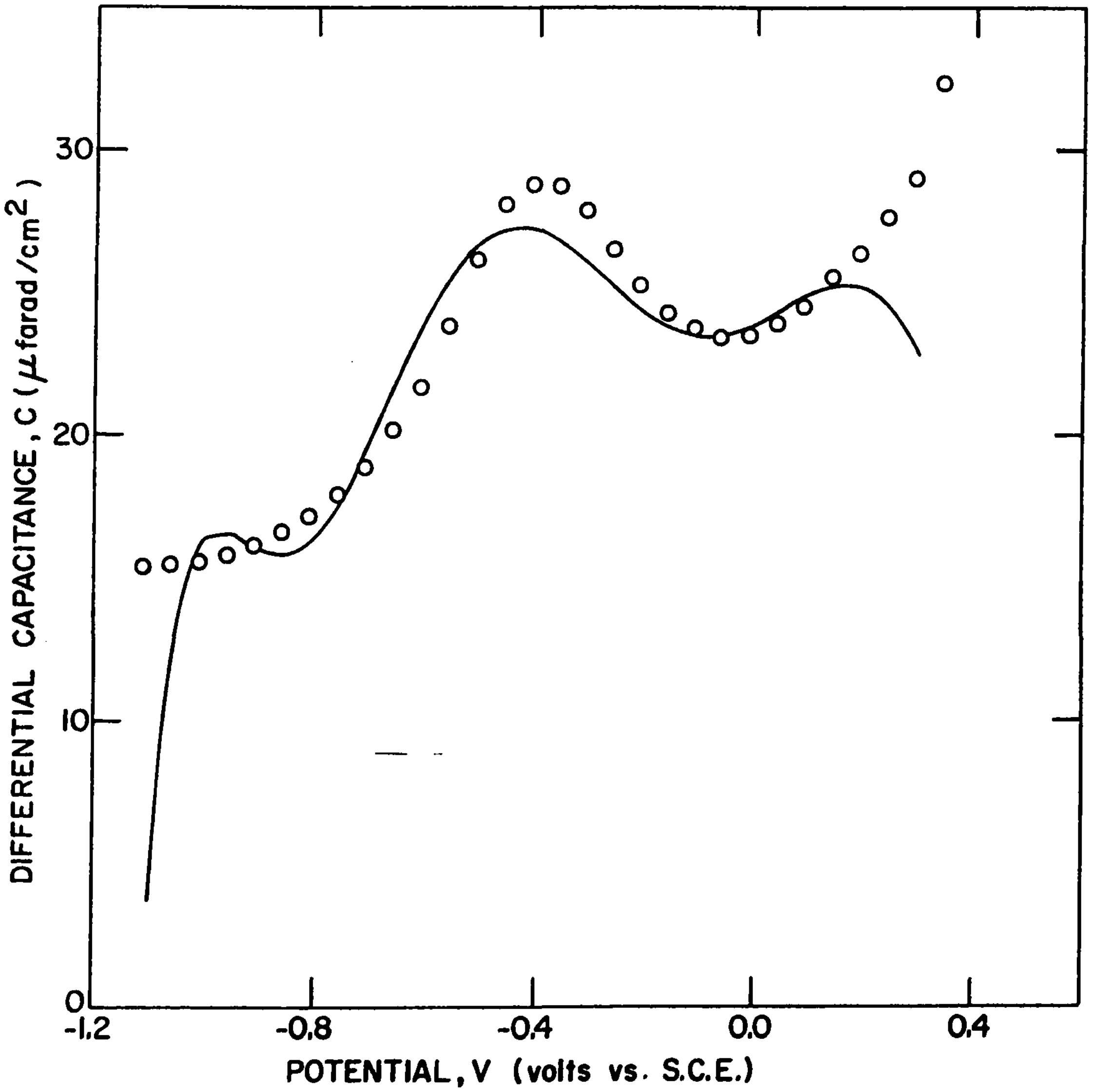

DIFFERENTIAL CAPACITANCE, C (μ farad/cm^2)
30
20
10
0
-1.2
-0.8
-0.4
0.0
0.4
POTENTIAL, V (volts vs. S.C.E.)

Figure 6. Electrocapillary curves for 3-pentanol in 0.100N $HClO_4$. Concentrations of 3-pentanol are (A) zero; (B) 0.0131M; (C) 0.0263M; (D) 0.0525M; (E) 0.133M; (F) 0.263M; (G) 0.588M.

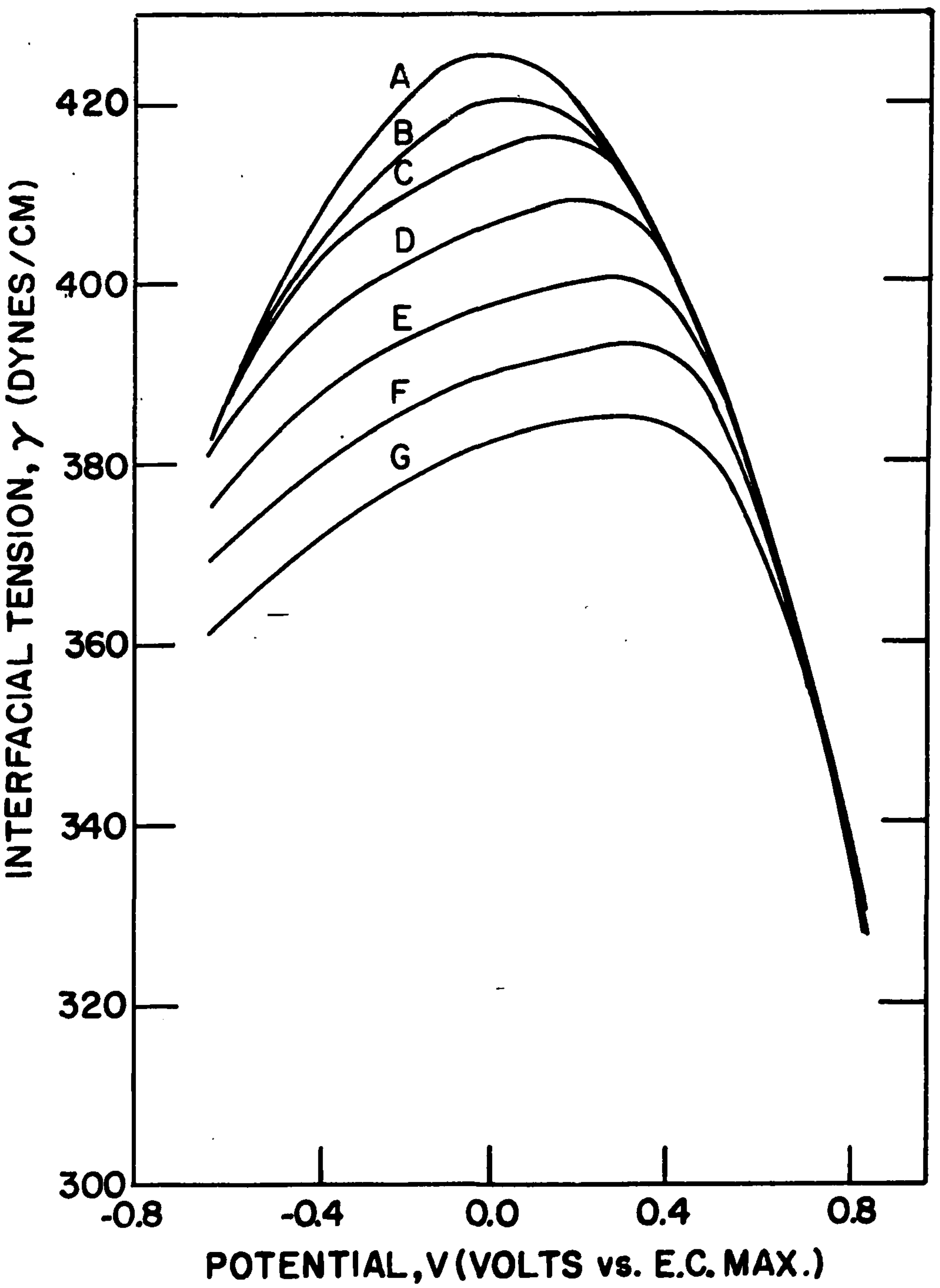

INTERFACIAL TENSION, γ (DYNES/CM)
300
320
340
360
380
400
420
-0.8
-0.4
0.0
0.4
0.8
POTENTIAL, V (VOLTS vs. E.C. MAX.)
A
B
C
D
E
F
G

Figure 7. Electrocapillary curves for chloroform in 0.100N $HClO_4$. Concentrations of chloroform are, from the top curve down, zero; 0.0126M; 0.0178M; 0.0251M; 0.0316M; 0.0377M; 0.0455M; 0.0460M; and 0.0494M.

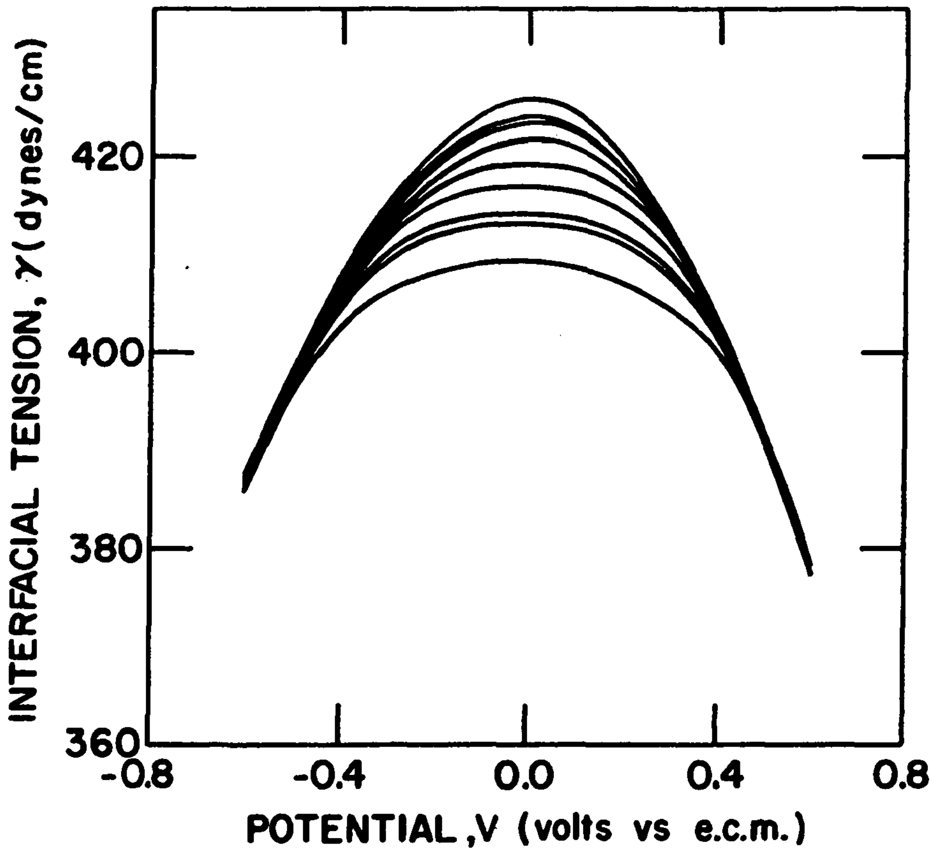

INTERFACIAL TENSION, γ(dynes/cm)
420
400
380
360
-0.8
-0.4
0.0
0.4
0.8
POTENTIAL ,V (volts vs e.c.m.)

Figure 8. Electrocapillary curves for cyclohexanol in 0.100N $HClO_4$. Activities of cyclohexanol are (A) zero; (B) 0.025; (C) 0.050; (D) 0.100; (E) 0.225; (F) 0.450; (G) 0.900.

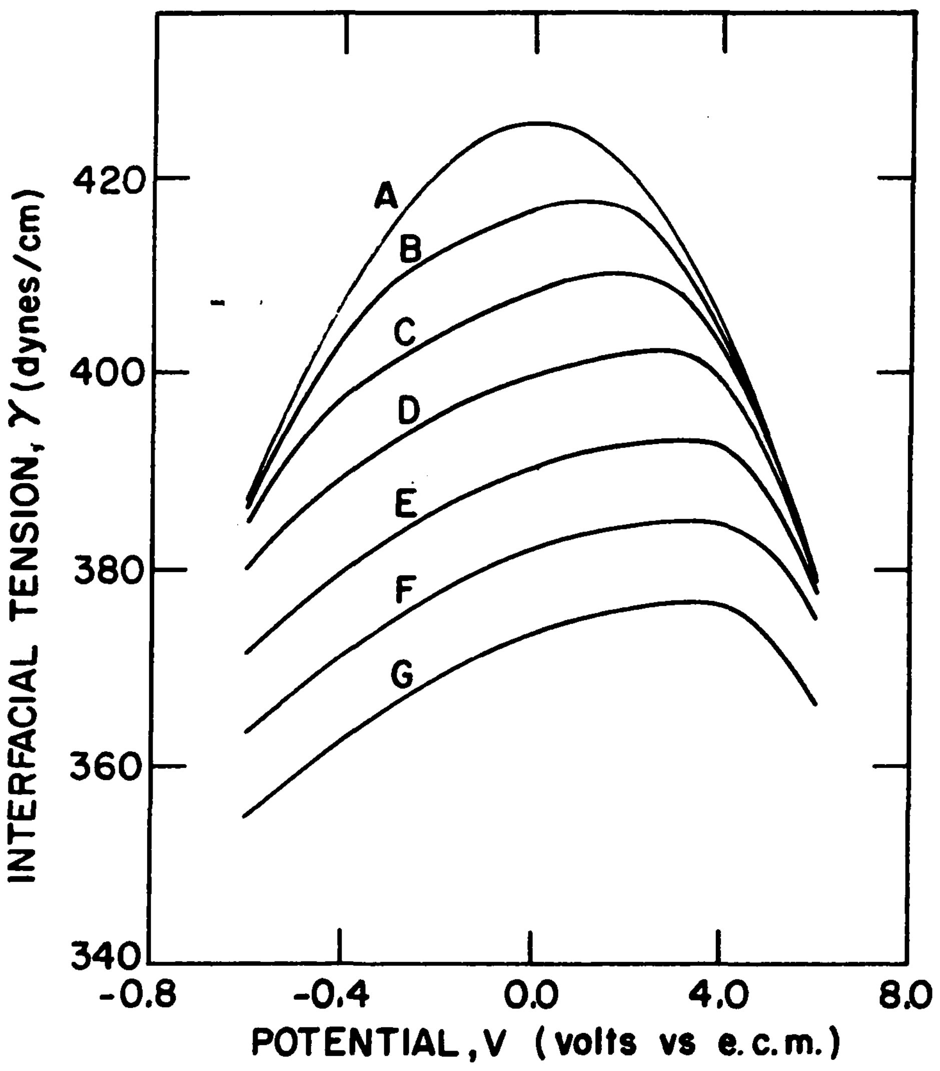

INTERFACIAL TENSION, γ (dynes/cm)
340
360
380
400
420
POTENTIAL, V (volts vs e.c.m.)
-0.8
-0.4
0.0
4.0
8.0
A
B
C
D
E
F
G

Figure 9. Electrocapillary curves for cyclohexanone in 0.100N $HClO_4$. Activities of cyclohexanone are (A) zero; (B) 0.025; (C) 0.050; (D) 0.100; (E) 0.238; (F) 0.475; (G) 0.950. Data for curves B and D were obtainable only for the regions shown. Data for curve C are unreliable to the left of the electrocapillary maximum.

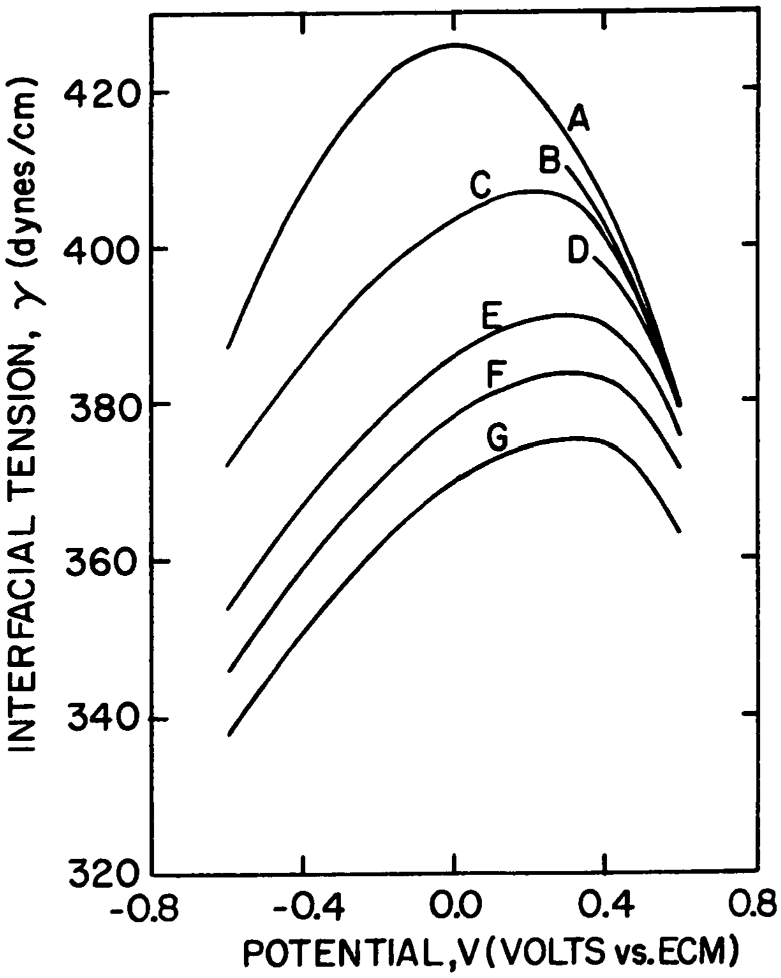

INTERFACIAL TENSION, γ (dynes/cm)
420
400
380
360
340
320
-0.8
-0.4
0.0
0.4
0.8
POTENTIAL,V(VOLTS vs.ECM)
A
B
C
D
E
F
G

Figure 10. Composite π-ln a curve for 3-pentanol. Points are experimental data; the line is calculated from the Frumkin equation fit to the data. In the legend above, the first number is the potential, V, in volts vs. the electrocapillary maximum potential for 0.100N $HClO_4$. The number in parenthesis is the amount by which the ln a axis has been shifted with respect to the curve for -0.033 volts.

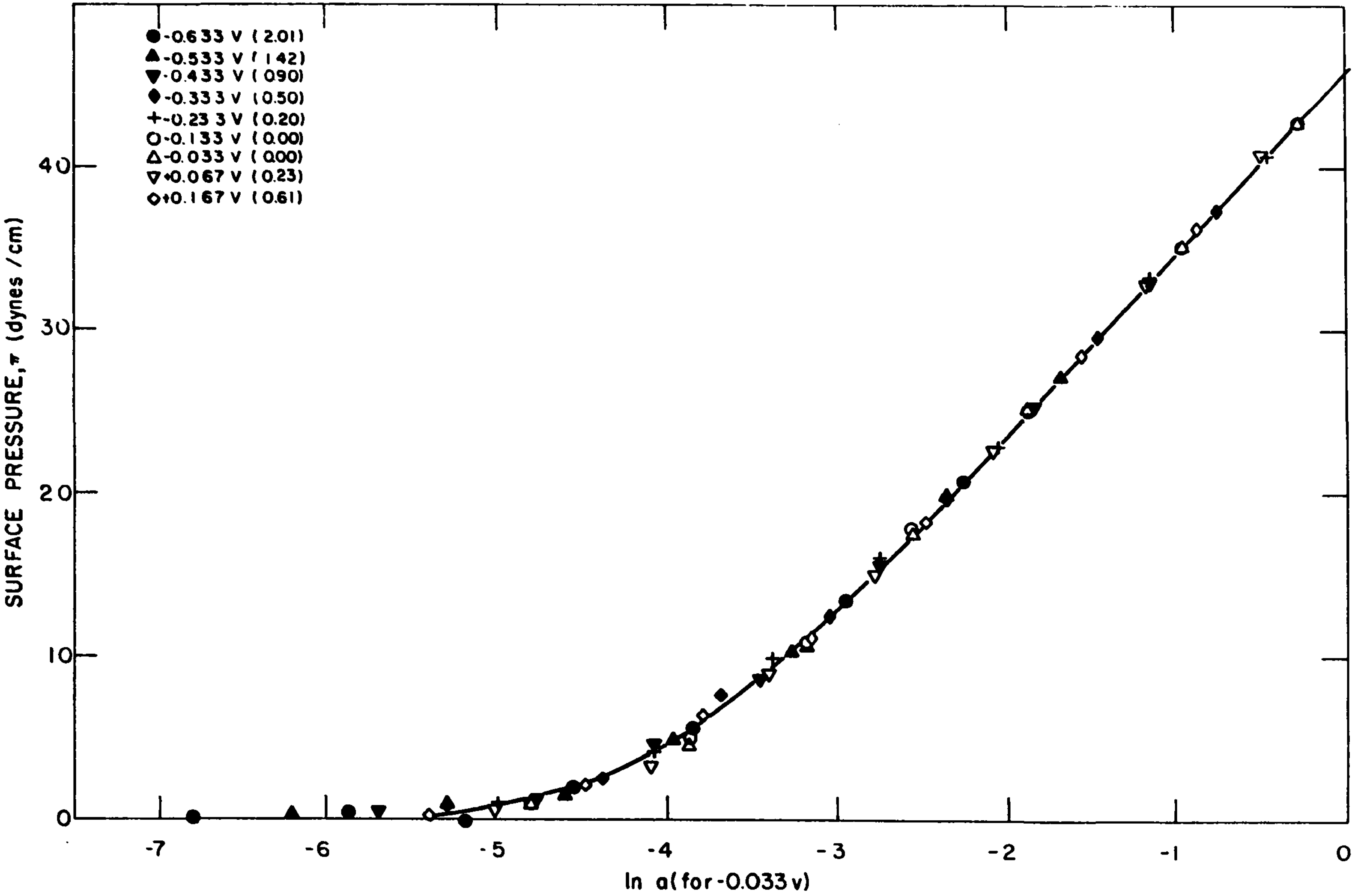
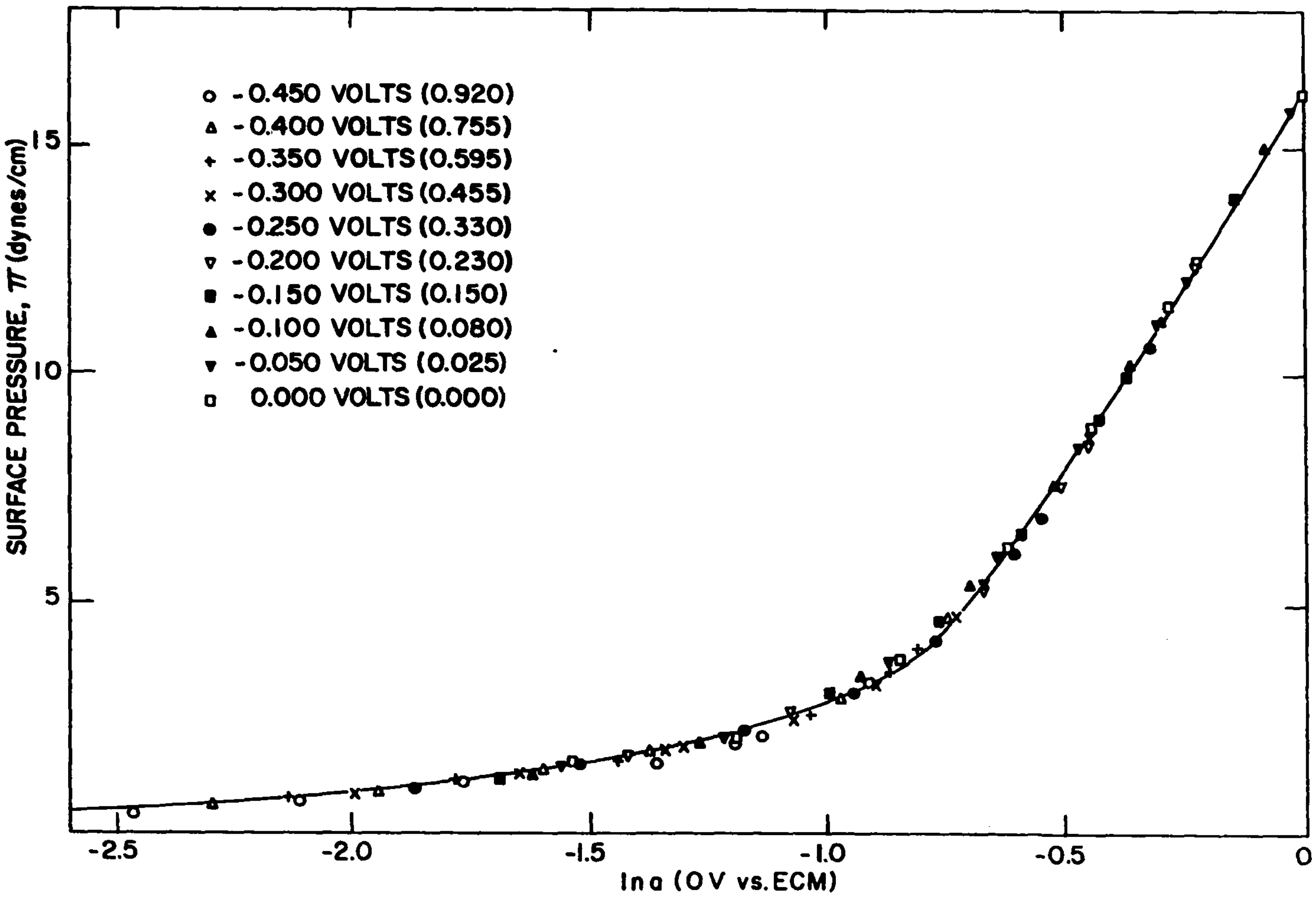

● -0.633 V (2.01)
▲ -0.533 V (1.42)
▼ -0.433 V (0.90)
◆ -0.333 V (0.50)
+ -0.233 V (0.20)
○ -0.133 V (0.00)
△ -0.033 V (0.00)
▽ +0.067 V (0.23)
◇ +0.167 V (0.61)
SURFACE PRESSURE, π (dynes /cm)
0
10
20
30
40
-7
-6
-5
-4
-3
-2
-1
0
ln a(for -0.033 v)

Figure 11. Composite π-ln a curve for chloroform. Legend as in Figure 10, except that the reference was the curve for 0 volts.



○ -0.450 VOLTS (0.920)
△ -0.400 VOLTS (0.755)
+ -0.350 VOLTS (0.595)
× -0.300 VOLTS (0.455)
● -0.250 VOLTS (0.330)
▽ -0.200 VOLTS (0.230)
■ -0.150 VOLTS (0.150)
▲ -0.100 VOLTS (0.080)
▼ -0.050 VOLTS (0.025)
□ 0.000 VOLTS (0.000)
SURFACE PRESSURE, π (dynes/cm)
15
10
5
-2.5
-2.0
-1.5
-1.0
-0.5
0
ln a (O V vs. ECM)

Figure 12. Composite π-ln a curve for cyclohexanol. Legend as in Figure 11.

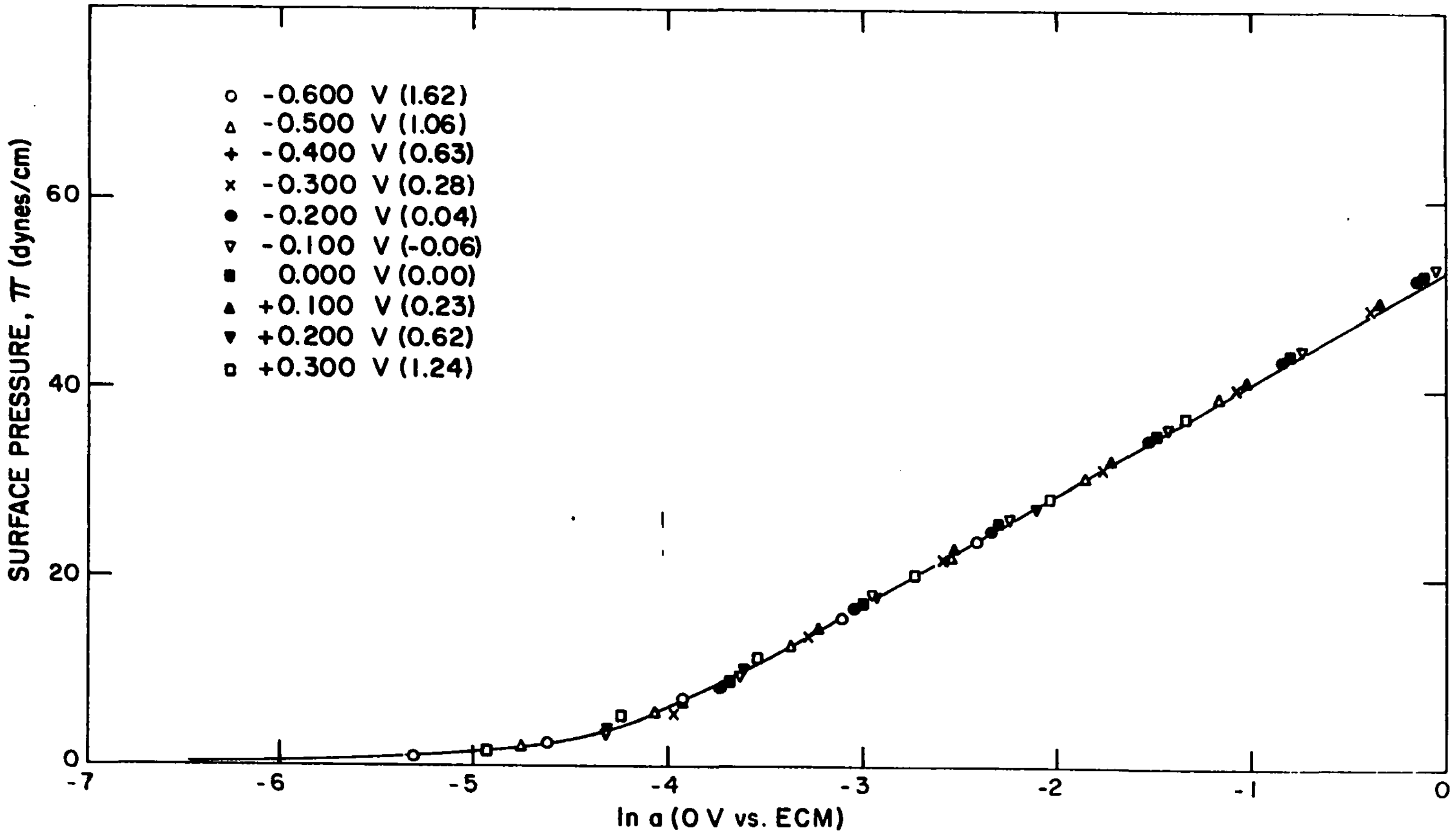

○ -0.600 V (1.62)
△ -0.500 V (1.06)
+ -0.400 V (0.63)
× -0.300 V (0.28)
● -0.200 V (0.04)
▽ -0.100 V (-0.06)
■ 0.000 V (0.00)
▲ +0.100 V (0.23)
▼ +0.200 V (0.62)
□ +0.300 V (1.24)
SURFACE PRESSURE, π (dynes/cm)
60
40
20
0
-7
-6
-5
-4
-3
-2
-1
0
ln a (0 V vs. ECM)

Figure 13. Composite π-ln a curve for cyclohexanone. Legend as in Figure 10, except that the potential, V, is in volts vs. S.C.E. and the reference was the curve for -0.7 volts.

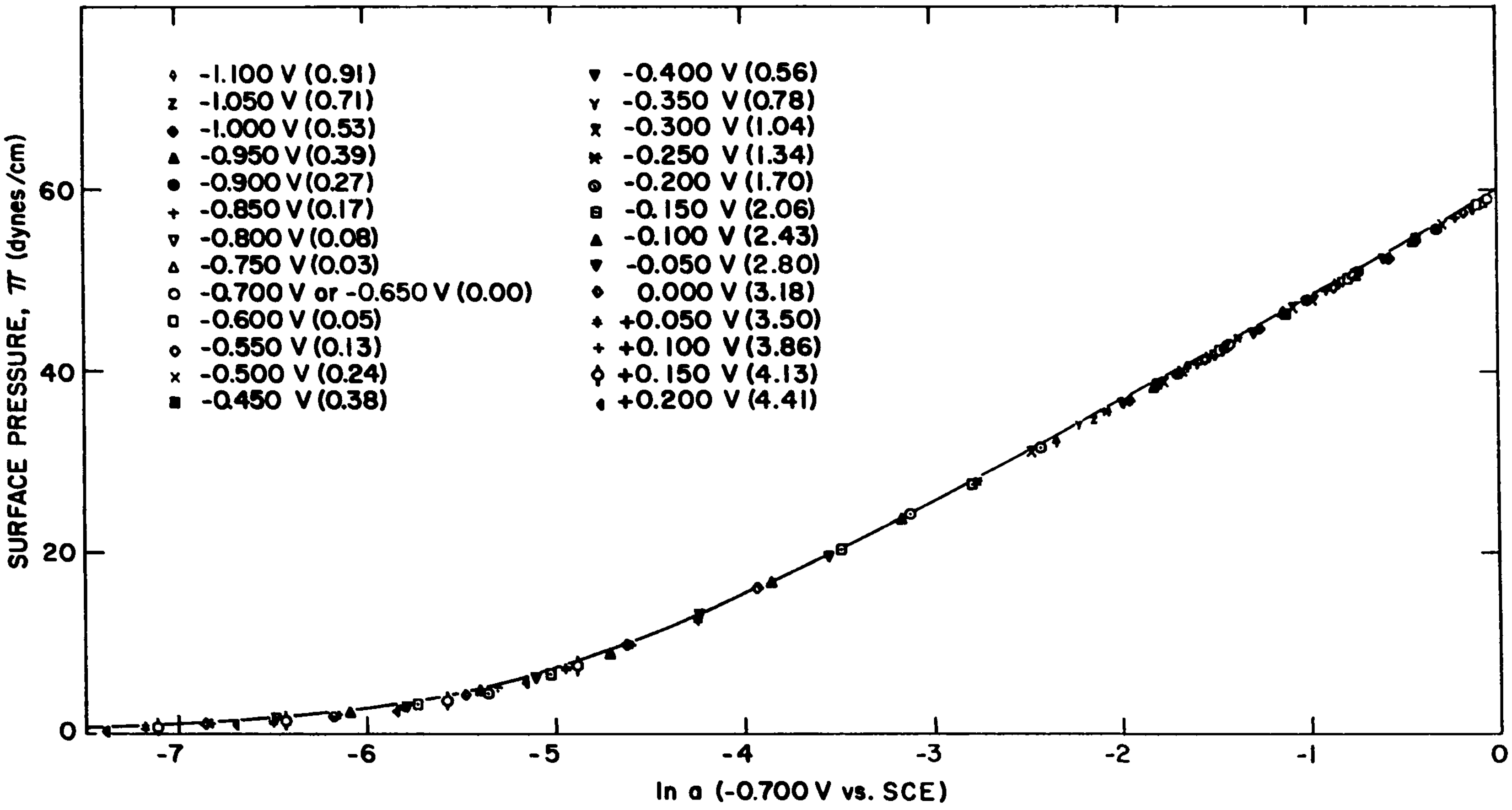

SURFACE PRESSURE, π (dynes/cm)
0
20
40
60
-7
-6
-5
-4
-3
-2
-1
0
ln a (-0.700 V vs. SCE)
-1.100 V (0.91)
-1.050 V (0.71)
-1.000 V (0.53)
-0.950 V (0.39)
-0.900 V (0.27)
-0.850 V (0.17)
-0.800 V (0.08)
-0.750 V (0.03)
-0.700 V or -0.650 V (0.00)
-0.600 V (0.05)
-0.550 V (0.13)
-0.500 V (0.24)
-0.450 V (0.38)
-0.400 V (0.56)
-0.350 V (0.78)
-0.300 V (1.04)
-0.250 V (1.34)
-0.200 V (1.70)
-0.150 V (2.06)
-0.100 V (2.43)
-0.050 V (2.80)
0.000 V (3.18)
+0.050 V (3.50)
+0.100 V (3.86)
+0.150 V (4.13)
+0.200 V (4.41)

Figure 14. ln a vs. θ curve for 3-pentanol. θ is the fractional surface coverage, Γ/Γ_m. Points shown were obtained by graphical differentiation of the composite π-ln a curve. The line is calculated from the Frumkin equation fit to the points.

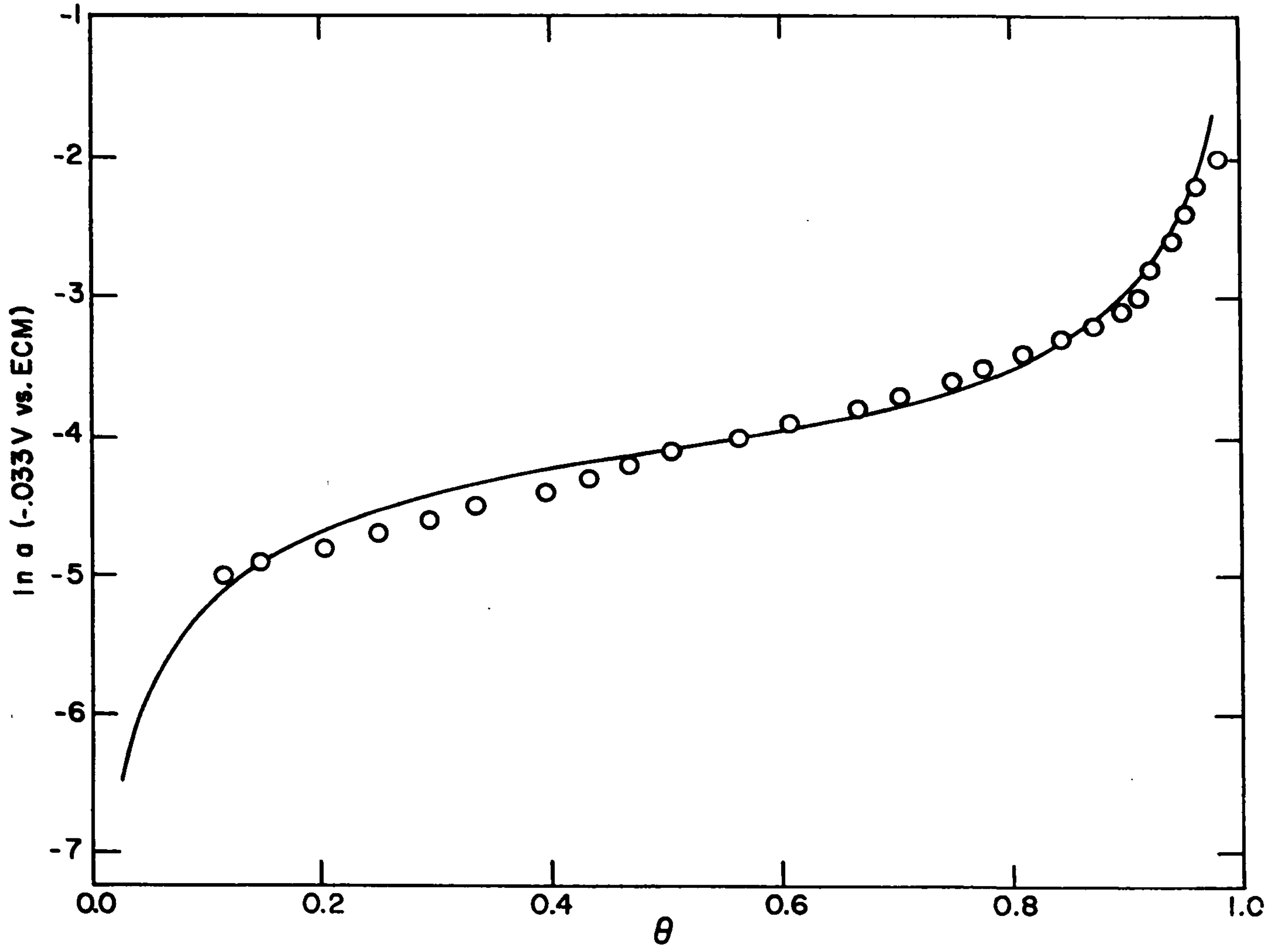

ln a (-.033V vs. ECM)
-1
-2
-3
-4
-5
-6
-7
0.0
0.2
0.4
0.6
0.8
1.0
θ

Figure 15. ln a vs. θ curve for chloroform.

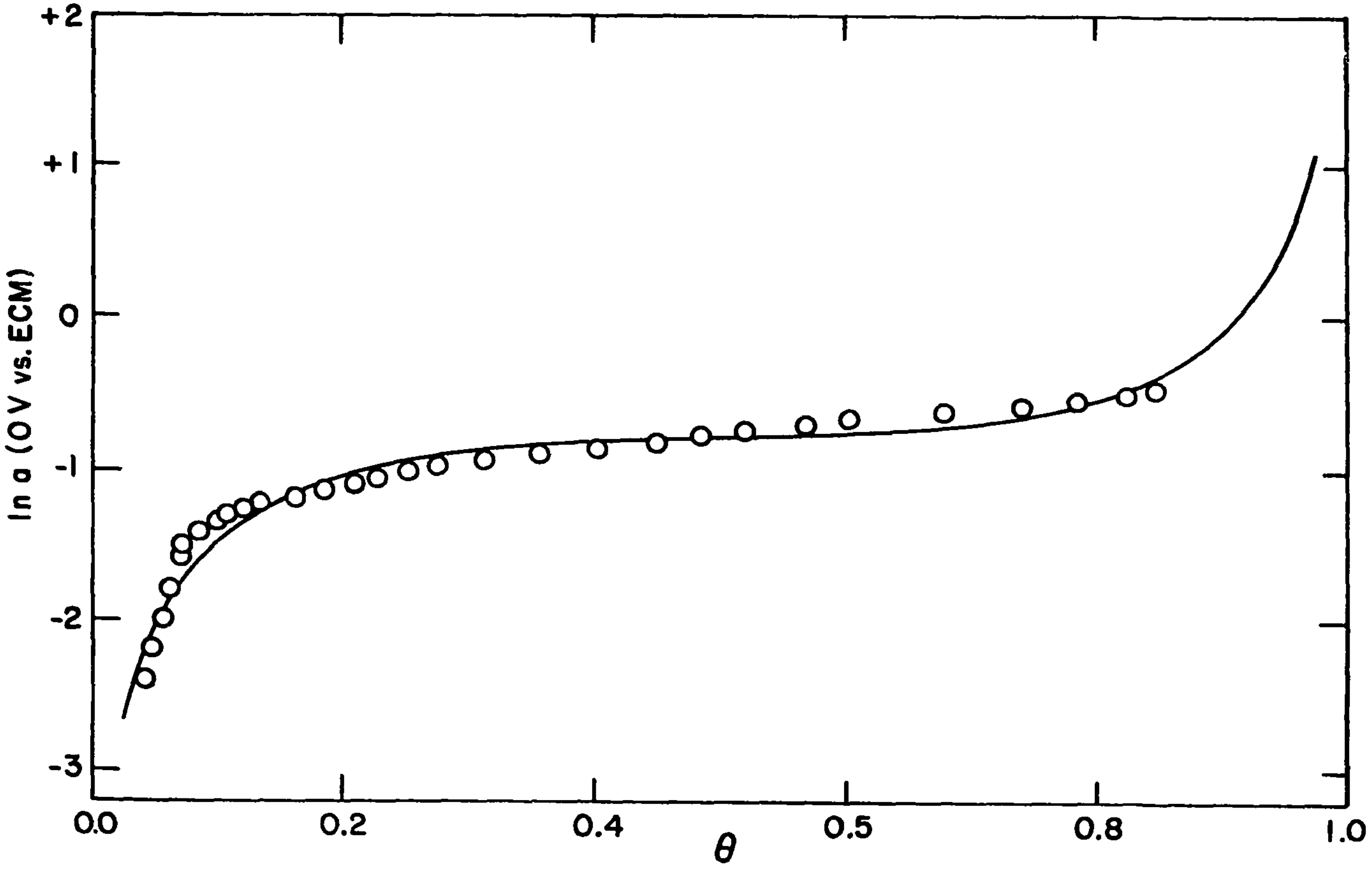

ln a (0 V vs. ECM)
+2
+1
0
-1
-2
-3
0.0
0.2
0.4
0.5
0.8
1.0
θ

Figure 16. ln a vs. θ curve for cyclohexanol.

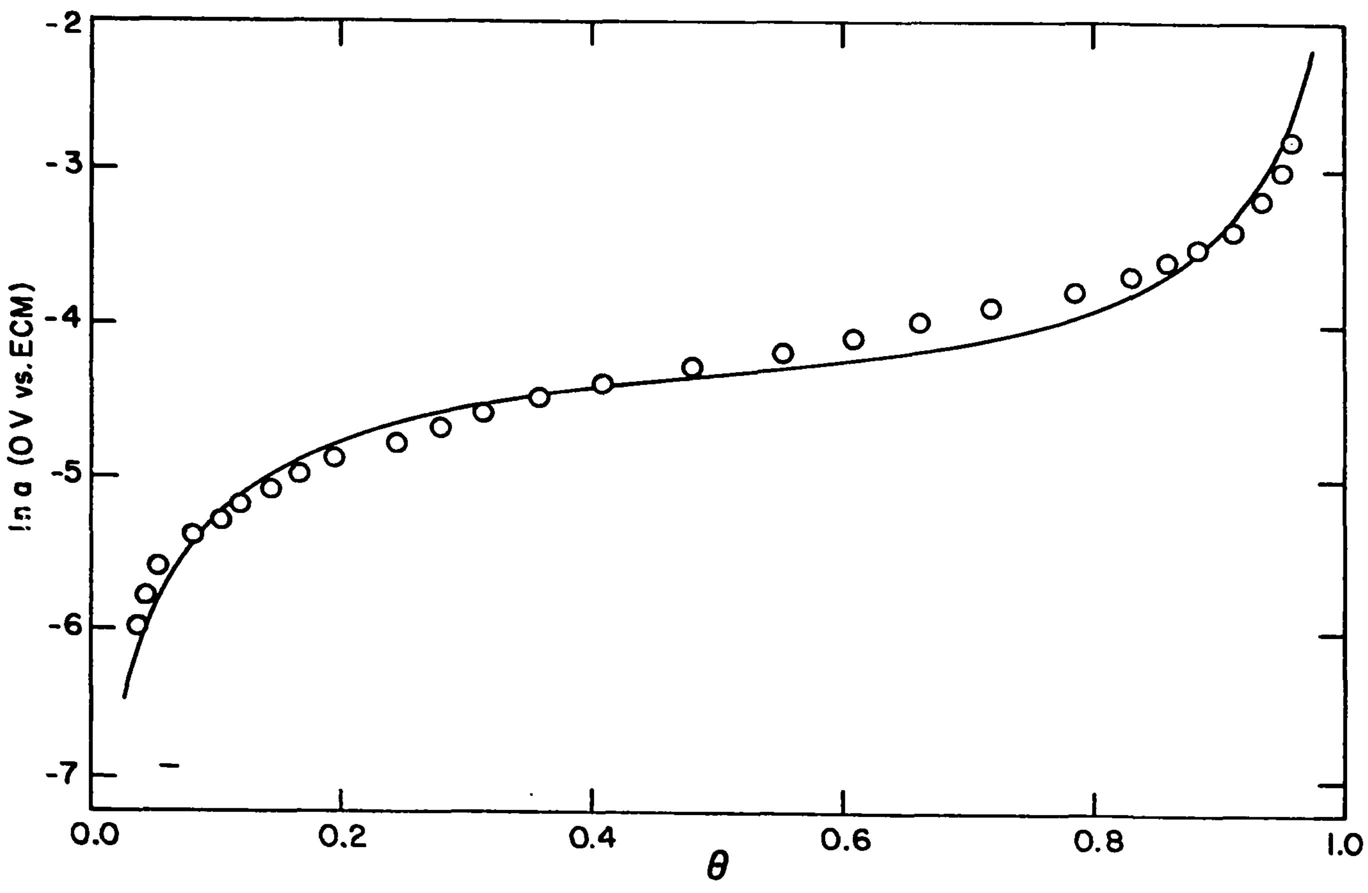

ln a (0 V vs. ECM)
-2
-3
-4
-5
-6
-7
0.0
0.2
0.4
0.6
0.8
1.0
θ

Figure 17. ln a vs. θ curve for cyclohexanone.

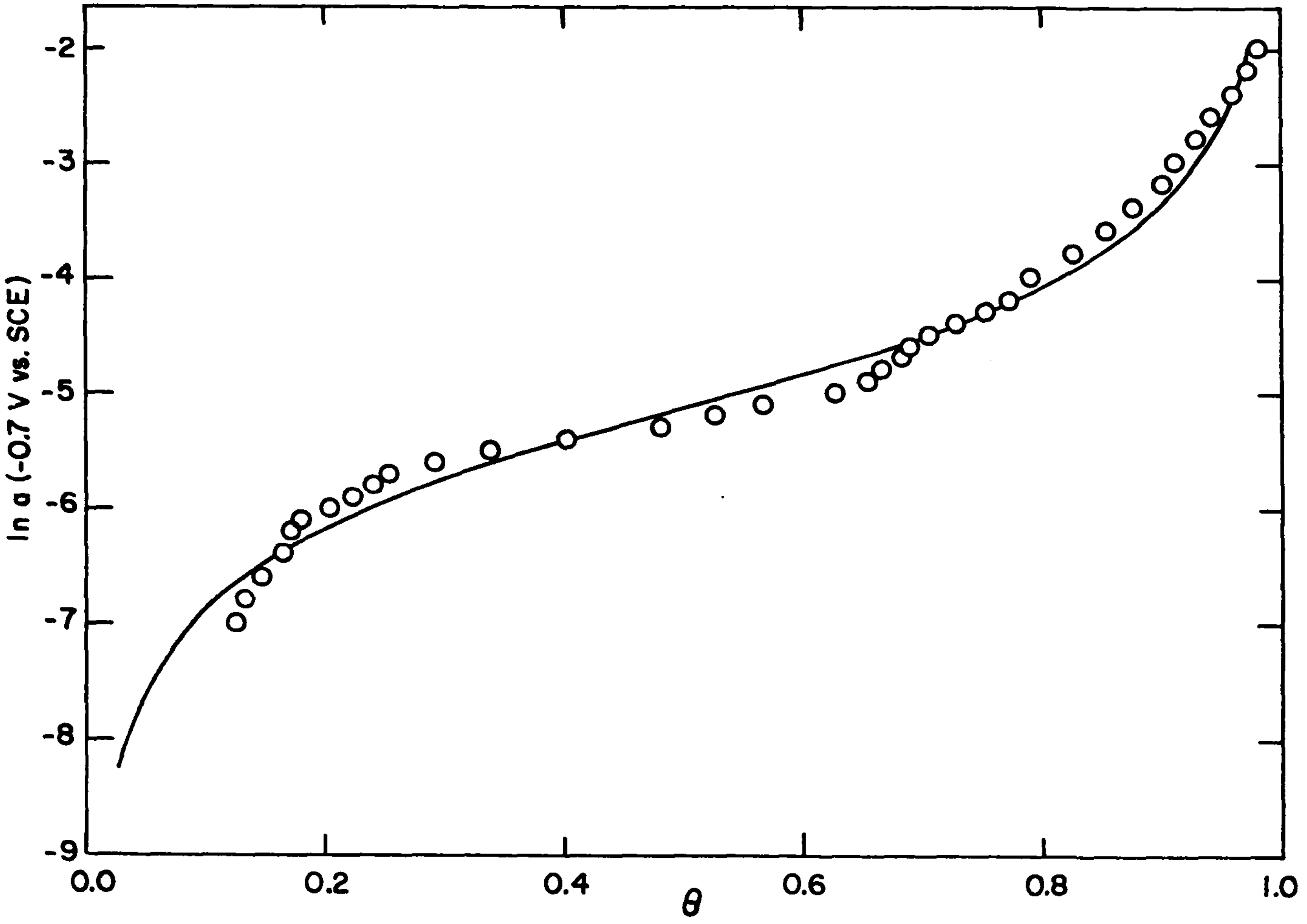

ln a (-0.7 V vs. SCE)
-2
-3
-4
-5
-6
-7
-8
-9
0.0
0.2
0.4
0.6
0.8
1.0
θ

Figure 18. Dimensionless adsorption isotherms. $a_{\frac{1}{2}}$ is the activity of the absorbate at which $\theta = \frac{1}{2}$. Adsorbates shown are (A) chloroform, (B) cyclohexanol, (C) 3-pentanol, and (D) cyclohexanone.

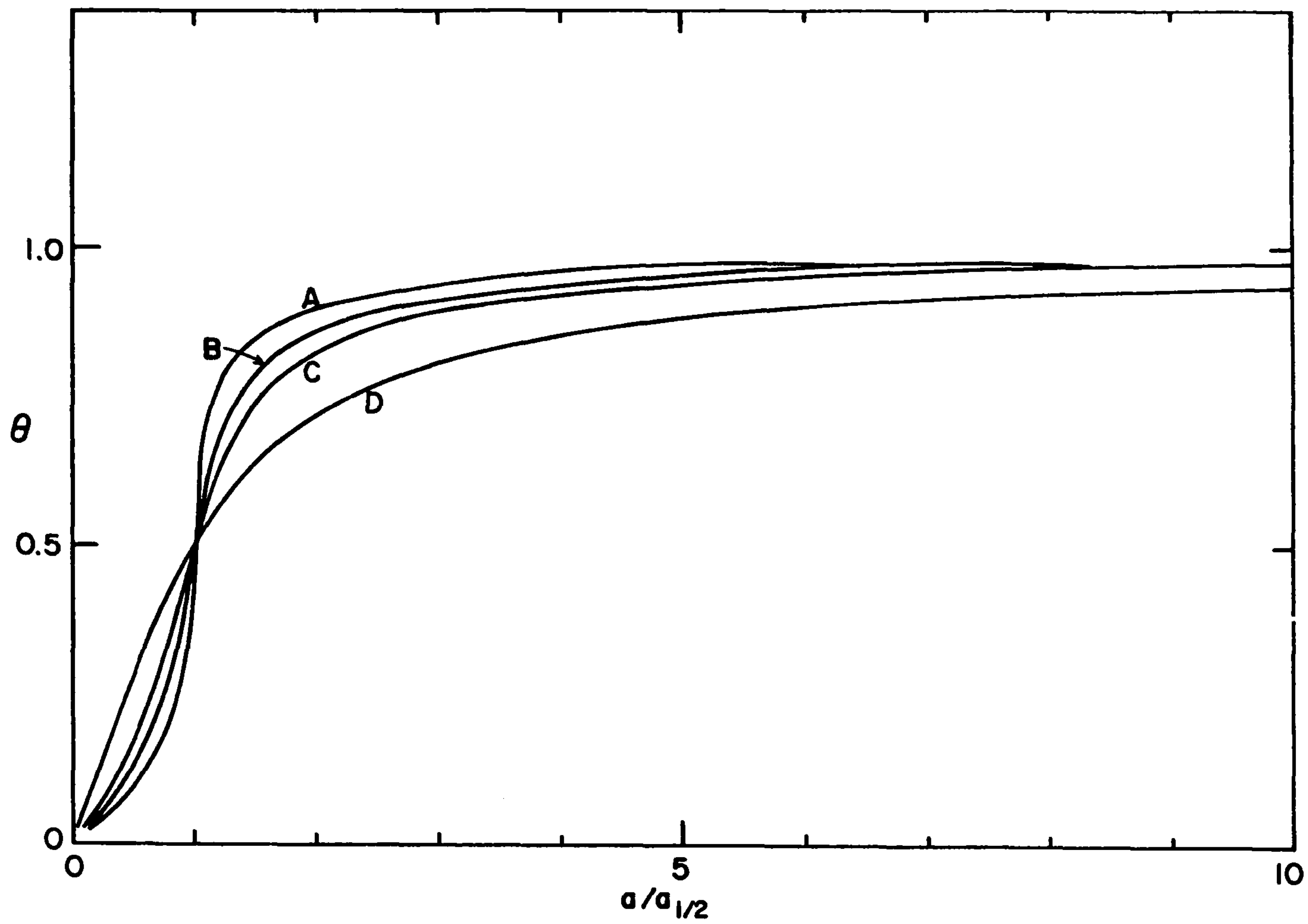

θ
1.0
0.5
0
0
5
10
a/a1/2
A
B
C
D

Figure 19. Standard free energy of adsorption referred to infinite dilution based standard states both in solution and on the surface. Adsorbates shown are (A) cyclohexanone, (B) cyclohexanol, (C) 3-pentanol, and (D) chloroform.

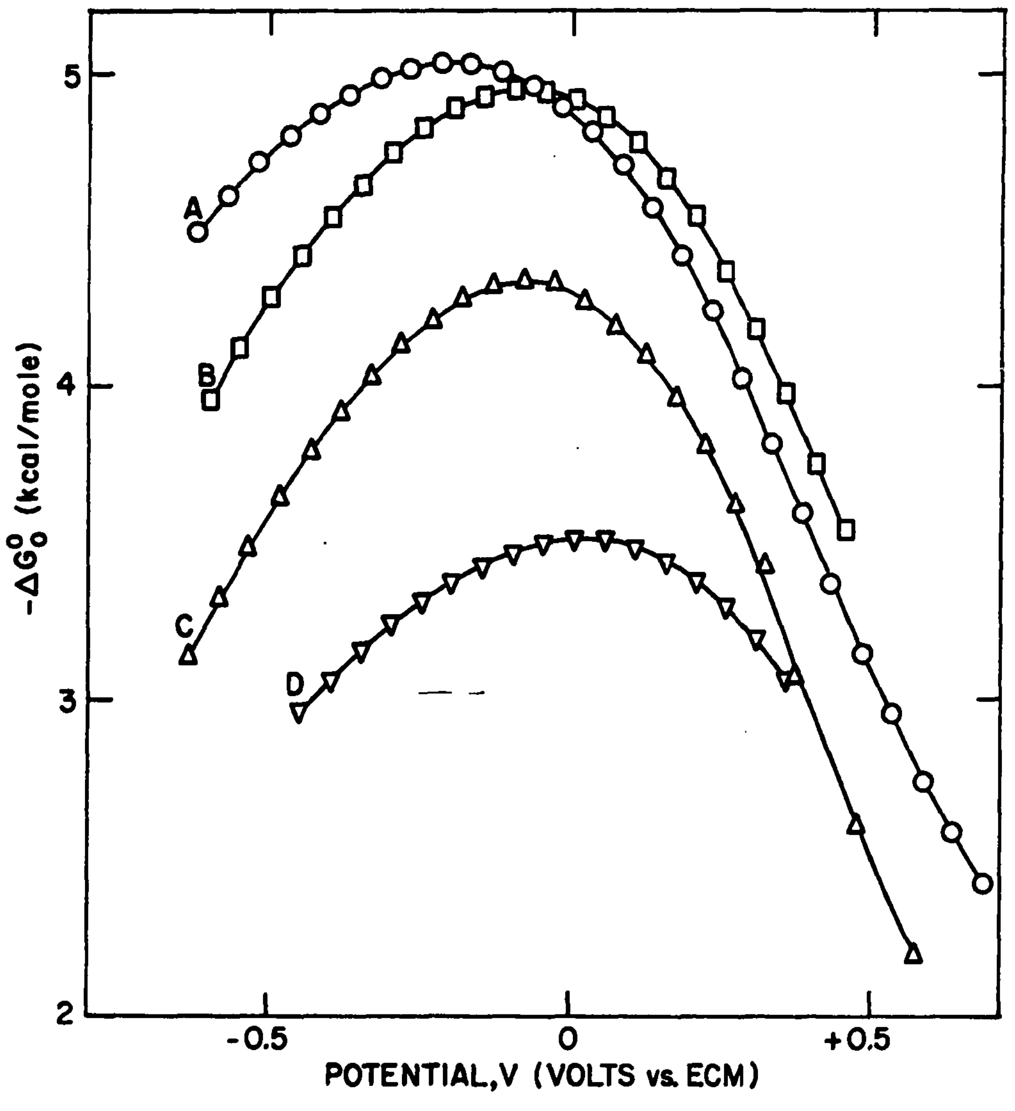

-ΔG$^0_0$ (kcal/mole)
5
4
3
2
A
B
C
D
-0.5
0
+0.5
POTENTIAL, V (VOLTS vs. ECM)

Figure 20. Standard free energy of adsorption referred to pure solute based standard states both in solution and on the surface. Adsorbates shown are (A) cyclohexanone, (B) cyclohexanol, (C) 3-pentanol, and (D) chloroform.

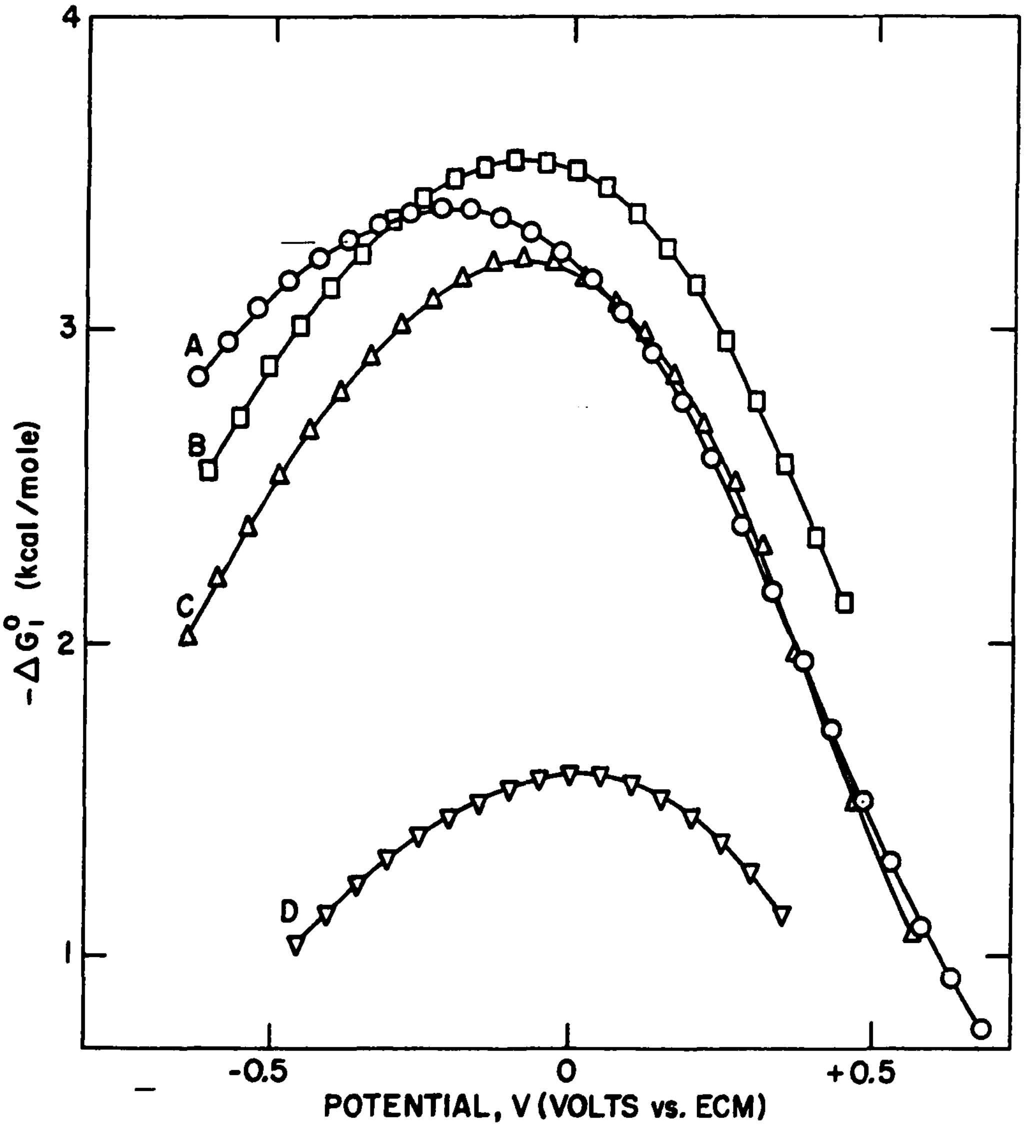

4
3
2
1
A
B
C
D
$-\Delta G_1^0$ (kcal/mole)
-0.5
0
+0.5
POTENTIAL, V (VOLTS vs. ECM)

Figure 21. Correlation of ΔG_o^o with polarizability, $\alpha = \frac{n_D^2-1}{n_D^2+2}\bar{V}$. Units of abscissa are cm mole$^{-1/3}$. Units of ordinate are cal cm^{-2} mole$^{-1/3}$. Points obtained in this study are (1) 3-pentanol, (2) chloroform, (3) cyclohexanol, and (4) cyclohexanone; Points obtained by previous workers in this laboratory from differential capacitance measurements are (5) 1-pentanol, (6) 3-pentanone, (7) 2,4-pentanedione, (8) pentanoic acid (9) pentanenitrile, (10) octanoic acid, (11) phenol.

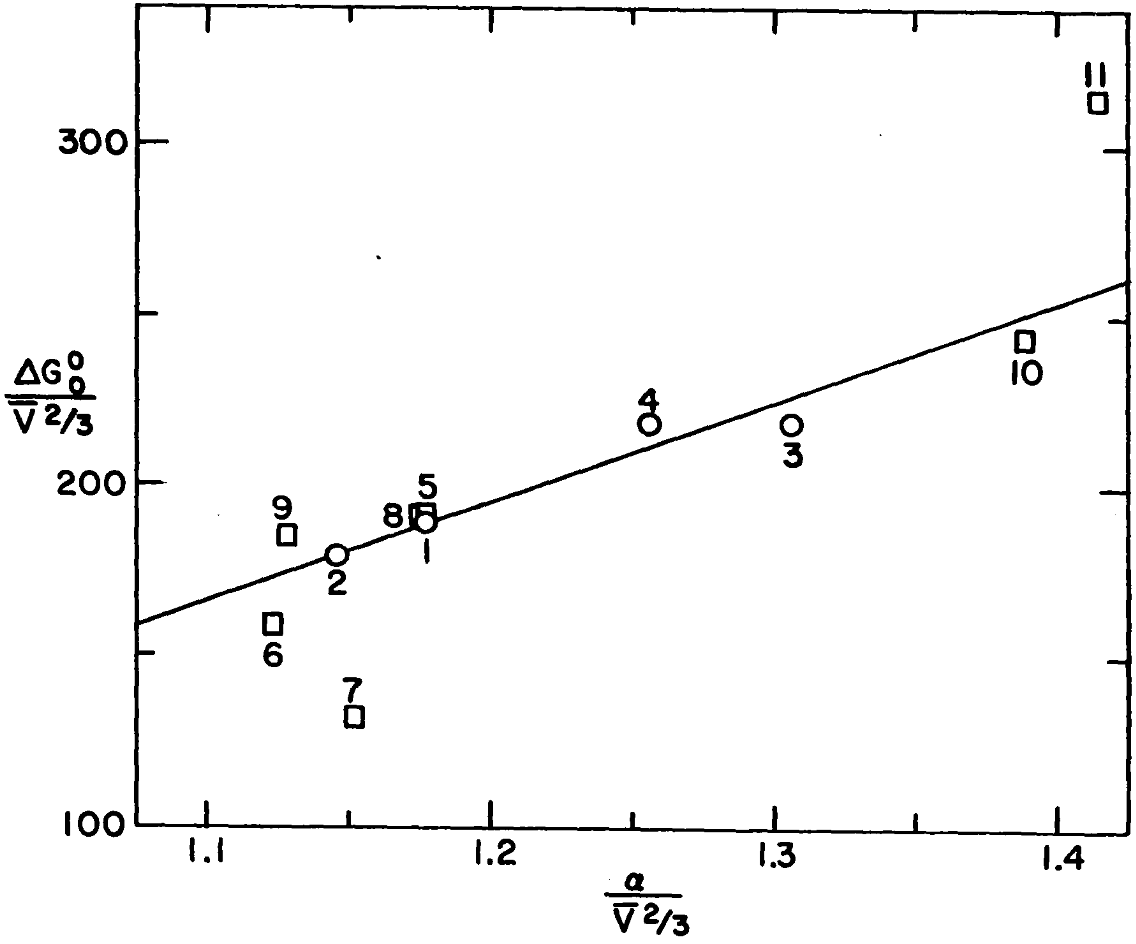
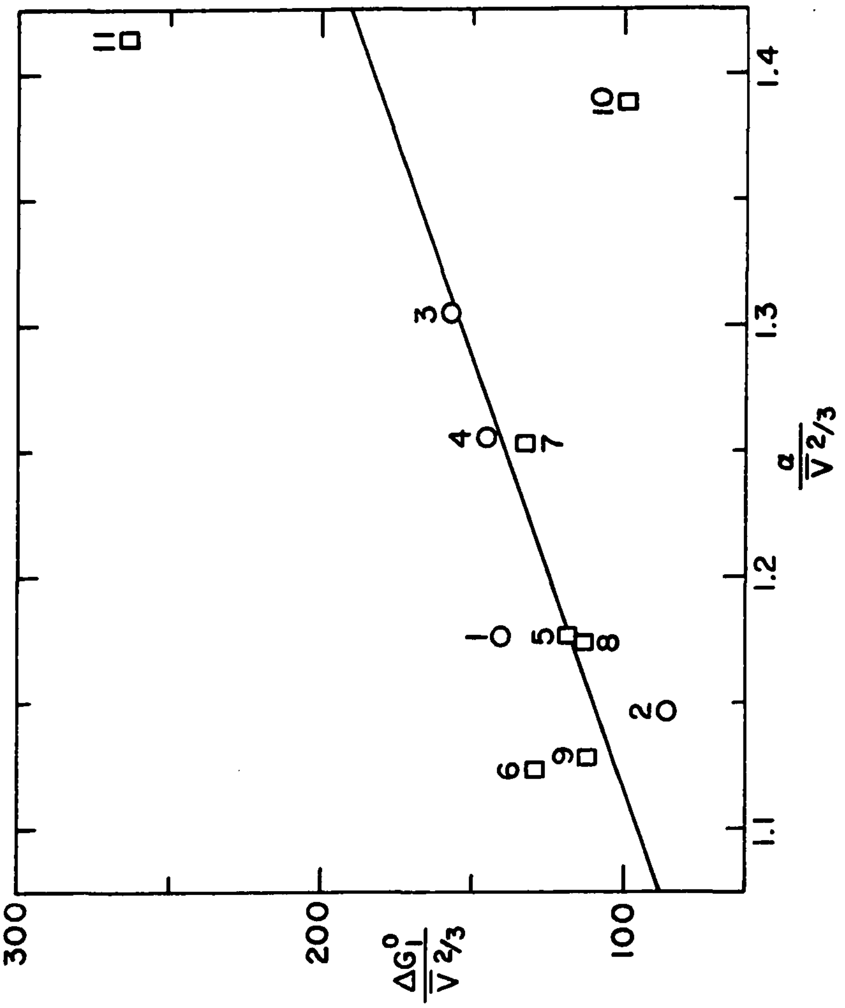

300
200
100
$\frac{\Delta G_0^0}{\bar{V}^{2/3}}$
1.1
1.2
1.3
1.4
$\frac{a}{\bar{V}^{2/3}}$
1
2
3
4
5
6
7
8
9
10
11

Figure 22. Correlation of ΔG_1^o with polarizability, α. Points are numbered as in Figure 21.


300
200
100
$\frac{\Delta G_1^0}{V^{2/3}}$
1.1
1.2
1.3
1.4
$\frac{a}{V^{2/3}}$
1
2
3
4
5
6
7
8
9
10
11

APPENDIX B

Computer Program Listings

```
C     PROGRAM FOR INITIAL ANALYSIS OF ELECTROCAPILLARY DATA
C
C        USE OF PROGRAM
C          RAW ELECTROCAPILLARY DATA FOR THE PROGRAM MAY BE OF
C          THREE TYPES, AS INDICATED BY THE PARAMETER IDATA.
C            IDATA = 1  GAS PRESSURE MEASURED WITH MANOMETER
C                  = 2  GAS PRESSURE MEASURED WITH BOURDON
C                       TUBE PRESSURE GAUGE
C                  = 3  DATA ALREADY CONVERTED TO DYNES/CM
C          THE PROGRAM MAY BE USED TO CALCULATE THE RADIUS OF
C          THE CAPILLARY IF DATA ARE TAKEN FOR A SOLUTION OF
C          KNOWN ELECTROCAPILLARY MAXIMUM, OR IT MAY BE USED
C          TO CALCULATE THE INTERFACIAL TENSION AT EACH DATA
C          POINT IF THE RADIUS IS ALREADY KNOWN.
C            ICALIB = 0  DATA ARE NOT FOR CALIBRATION; RADIUS
C                        = RADIUS OF CAPILLARY IN CM.
C            ICALIB = 1  DATA ARE FOR CALIBRATION OF
C                        CAPILLARY; RADIUS = E.C.MAX. OF
C                        SOLUTION (DYNES/CM).
C
C        METHOD
C          THE PROGRAM FIRST FINDS THE PRESSURE ON THE
C          INTERFACE FOR EACH DATA POINT (IF IDATA = 1 OR 2),
C          AND THEN CONVERTS THIS TO INTERFACIAL TENSION (IF
C          ICALIB = 0).  IN EITHER CASE, WHETHER THE FINAL
C          RESULTS ARE PRESSURE OR INTERFACIAL TENSION, THE
C          ARRAY IS LAVELLED Y, AND THE DATA (VOLTS,Y) ARE
C          THEN FIT WITH A LEAST SQUARES POLYNOMIAL (FOR A
C          DEFINITION OF "BEST FIT", SEE SUBROUTINE FITECC).
C          WEIGHTING FACTORS ARE ASSIGNED TO EACH DATA POINT
C          BY FITTING THE DIFFERENCES BETWEEN EXPERIMENTAL
C          AND CALCULATED Y'S WITH A NORMAL ERROR CURVE, AND
C          THE DATA ARE FIT AGAIN USING THESE WEIGHTS.  A PLOT
C          OF THE CALCULATED ELECTROCAPILLARY CURVE WITH
C          SUPERIMPOSED EXPERIMENTAL POINTS IS MADE, AS WELL
C          AS A PLOT OF THE REGION NEAR THE E.C.MAX.  IF THE
C          DATA WERE NOT USED FOR A CALIBRATION, THE CHARGE
C          DENSITY, Q, AND THE DIFFERENTIAL CAPACITANCE OF THE
C          DOUBLE LAYER, C, ARE CALCULATED FROM THE POLYNOMIAL
C          FIT AND PLOTTED, AND THE COEFFICIENTS OF THE
C          POLYNOMIAL ARE PUNCHED ON DATA CARDS FOR USE IN THE
C          NEXT PROGRAM.  IF THE DATA WERE USED FOR A
C          CALIBRATION, THE RADIUS OF THE CAPILLARY IS FOUND.
C
C        DESCRIPTION OF DATA CARDS
C          ALL DATA MUST BE IN CGS UNITS, UNLESS OTHERWISE
C          NOTED.
C          INITIAL CARDS (ONLY ONE SET, AT BEGINNING OF RUN):
C            CARD 1 (3F10.0):  GRAV - ACCELERATION OF GRAVITY,
C              DHG - DENSITY OF MERCURY, DH2O - DENSITY OF
```

```
C              WATER.
C           CARD 2 (2F15.0):  BOURD(1) AND BOURD(2) - COEFS.
C              (IN ASCENDING POWER OF DOD) OF THE LINEAR
C              APPROX. TO THE BOURDON TUBE CONSTANT, IN INCHES
C              OF HG PER DEGREE OF DEFLECTION.
C           CARD 3 (3F10.0):  CMICR - CALIBRATION CONSTANT OF
C              THE MICROSCOPE RETICLE USED TO POSITION THE HG
C              SURFACE IN THE CAPILLARY, IN CM/DIVISION, DIV -
C              DISTANCE OF HG SURFACE FROM BOTTOM OF
C              CAPILLARY, IN DIVISIONS ON MICROSCOPE RETICLE,
C              RADIUS - EXPLAINED ABOVE.
C           CARD 4 (5A4): XL - X-LABEL FOR GRAPHS (UNITS OF
C              POTENTIAL)
C           CARD 5 (3I5): IDATA, ICALIB, MSTART - LOWEST
C              DEGREE POLYNOMIAL TO BE FIT TO DATA.
C         CARDS FOR EACH DATA SET:
C           CARDS 6 & 7 (20A4/20A4):  TITLE
C           CARD 8 (15A4):  ORG, ELECTR, DATE - TITLES FOR
C              GRAPHS (MUST BE 20 CHARACTERS EACH, STARTING IN
C              COLUMNS 1, 21, AND 41).
C           CARD 9 (4F10.0):  (OMIT IF IDATA = 3)  TOPHG,
C              WATER, BOTCAP - CATHETOMETER READINGS OF THE
C              TOP OF THE HG COLUMN BEFORE DATA WAS TAKEN, THE
C              LEVEL OF THE SOLUTION IN THE CELL, AND THE
C              BOTTOM OF THE CAPILLARY, CORR - DECREASE IN HG
C              HEIGHT PER DROP OF HG EXPELLED.
C           CARDS 10 TO (N-2) (4F10.0):  DATA FOR EACH POINT
C              OF THE ELECTROCAPILLARY CURVE (MUST BE IN ORDER
C              FROM SMALLEST TO LARGEST POTENTIAL.  NEED NOT
C              BE EVENLY SPACED.).
C              IF IDATA = 1:  VOLTS - APPLIED POTENTIAL,
C              MANTOP - READING OF TOP MANOMETER COLUMN,
C              MANBOT - READING OF BOTTOM MANOMETER COLUMN,
C              DROPS - NO. OF DROPS OF HG EXPELLED SO FAR.
C              IF IDATA = 2:  VOLTS, DOD - DEGREES OF
C              DEFLECTION ON BOURDON TUBE PRESSURE GAUGE,
C              DROPS.
C              IF IDATA = 3:  VOLTS, Y - INTERFACIAL TENSION
C           CARD (N-1):  BLANK CARD, TO INDICATE END OF ABOVE
C              ARRAY.
C           CARD N (I5):  NDATA - NUMBER OF THE DATA SET
C              (LAST DATA SET MUST HAVE NDATA = 0).
C
C
      COMMON  NPTS, VOLTS(100), Y(100), W(100), YCOF(11),
     1        DYCOF(10), DDYCOF(9), RMS, WTRMS, VMAX, YMAX,
     2        MDEG, YEST(100), ERROR(100), ORG(5), ELECTR(5),
     3        WTFACT(5), DATE(5), MSTART, Z
      DIMENSION  TDEG(10), DEG(5), TYLP(5), TYLG(5), TWTF1(5),
     1           TWTF2(5), GL(5), SCALE(5), GLQ(5), YLQ(5),
```

```
     2            GLC(5), YLC(5), BOURD(2), XL(5), TITLE(40),
     3            DROPS(100), DOD(10C), YL(5), VEXP(100),
     4            YEXP(100), YESTEX(100), QCOF(10), CCOF(9),
     5            Q(100), C(10C)
      INTEGER Z, $
      REAL  MANTOP(100), MANBOT(100)
      EQUIVALENCE  (MANTCP,DOD,Q,VEXP), (MANBOT,C,YEXP),
     1             (DROPS,W), (DYCOF,QCOF), (DDYCOF,CCOF)
C
C
 1001 FORMAT (4F10.0)
 1002 FCRMAT (2F15.0)
 1003 FORMAT (20A4/20A4)
 1004 FORMAT (3I5)
 2001 FORMAT (15A4)
 2CC2 FORMAT (1P4E15.7)
 3001 FORMAT ('1'////1X,20A4/2X,20A4)
 3002 FORMAT (//'  INPUT PARAMETERS')
 3003 FORMAT (/4X,'GRAV',6X,'DHG',8X,'DH20'/F10.2,F11.4,F11.5)
 3004 FORMAT (/4X,'BOURC(1)',8X,'BOURC(2)'/2F16.6)
 3005 FORMAT (/4X,'CMICR',6X,'DIV',4X,'RADILS'/F11.5,F7.1,
     1 1PE14.4)
 3006 FORMAT (/4X,'XL'/4X,5A4)
 3007 FORMAT (/4X,'IDATA',4X,'ICALIB',4X,'MSTART'/I5,I9,I10)
 3008 FORMAT (/4X,'ORG',20X,'ELECTR',17X,'DATE'/4X,5A4,3X,5A4,
     1 3X,5A4)
 3C09 FORMAT (///'  DATA PCINTS (GAS PRESSURE MEASURED WITH ',
     1 'MANOMETER)')
 3010 FORMAT (/6X,'TOPHG',5X,'WATER',5X,'BOTCAP',7X,'CCRR'/
     1 F12.3,2F10.3,F14.7)
 3011 FORMAT (/6X,'VOLTS',4X,'MANTOP',4X,'MANBCT',4X,'DROPS'/
     1 (F11.3,2F10.3,F8.0))
 3012 FCRMAT (///'  DATA POINTS (GAS PRESSURE MEASURED WITH ',
     1 'BOURCON GAUGE)')
 3013 FCRMAT (/6X,'VOLTS',6X,'DOD',6X,'DROPS'/(2F11.3,F8.0))
 3014 FCRMAT (///'  DATA PCINTS (IN DYNES/CM)')
 3015 FORMAT (/6X,'VOLTS',7X,'Y'/(2F11.3))
 3016 FORMAT ('1'////' OUTPUT CATA'/'  VOLTS = EMF IN ',5A4/
     1 6X,'Y = ',5A4)
 3C17 FORMAT ('1'////' BEST FIT TO CATA FOR ',5A4,1X,5A4,1X,
     1 5A4/1X,5A4)
 3018 FORMAT (/'  PCLYNCMIAL OF CEGREE ',I2,' WAS BEST FIT.'/
     1 '  RMS CEVIATION = ',F5.3)
 3019 FORMAT (/5X,'VOLTS',4X,'Y(EXPTL)',4X,'Y(CALCD)',5X,
     1 'ERROR'/(F10.3,F11.3,F12.3,F11.3))
 3020 FORMAT ('1')
 3021 FORMAT (/5X,'VCLTS',4X,'WEIGHT',4X,'Y(EXPTL)',4X,
     1 'Y(CALCD)',5X,'ERROR',7X,'Q',8X,'C'/(F10.3,F9.3,F12.3,
     2 F12.3,F11.3,F10.2,F9.2))
 3C22 FORMAT (/'  RADIUS OF CAFILLARY = ',1PE12.6)
```

```
 3023 FORMAT (/5X,'VOLTS',4X,'WEIGHT',4X,'Y(EXPTL)',4X,
     1 'Y(CALCD)',5X,'ERROR'/(F10.3,F9.3,F12.3,F12.3,F11.3))
 3024 FORMAT ('  COORDINATES OF ELECTROCAPILLARY MAXIMUM ARE '
     1 '(',F6.3,',',F7.3,')')
 3025 FORMAT ('  NO MAXIMUM WAS FOUND IN REGION OF DATA.')
C
C
C         PUT ALPHANUMERIC DATA INTO ARRAYS FOR GRAPH LABELS.
C
      DATA TDEG(3)/4H3RD /,TDEG(4)/4H4TH /,TDEG(5)/4H5TH /,
     Z     TDEG(6)/4H6TH /,TDEG(7)/4H7TH /,TDEG(8)/4H8TH /,
     1     TDEG(9)/4H9TH /,TDEG(10)/4H10TH/,DEG(2)/4H DEG/,
     2     DEG(3)/4H. PO/,DEG(4)/4HLYNO/,DEG(5)/4HMIAL/,
     3     TYLP /20HPRESSURE (CM OF HG) /,
     4     TYLG /20HGAMMA (DYNES/CM)    /,
     5     TWTF1/20H NO WEIGHTS USED    /,
     6     TWTF2/20H WEIGHTS WERE USED  /,
     7     GL   /20HE.C. CURVE FOR      /,
     8     SCALE/20HREGION NEAR E.C.MAX./,
     9     GLQ  /20HCHARGE ON HG        /,
     A     YLQ  /20HQ (MICROCOUL/CM**2) /,
     B     GLC  /20HCAPACITANCE OF D.L. /,
     C     YLC  /20HC (MICROFARAD/CM**2)/
C
C         WITH THE PROPER CONTROL CARDS, SETTING Z AND $ = 13
C         WILL CAUSE ALL WRITE STATEMENTS WITH A Z OR $ TO BE
C         OUTPUT ON THE PRINTER, AND WILL CAUSE ALL PROGRAM
C         INTERRUPT STATEMENTS NOT TO BE OUTPUT.  SETTING Z = 3
C         WILL CAUSE ALL WRITE STATEMENTS WITH A Z NOT TO BE
C         OUTPUT (USE FOR FINAL WHITE PAPER JOBS).
C
      Z = 3
      $ = 13
C
C         READ INITIAL DATA CARDS.
C
      READ (1,1001) GRAV,DHG,DH20
      READ (1,1002) BOURD(1),BOURD(2)
      READ (1,1001) CMICR,DIV,RADIUS
      READ (1,1003) XL
      READ (1,1004) IDATA,ICALIB,MSTART
C
C         READ TITLE, SYSTEM, DATE & PRINT ALL INPUT DATA SO
C         FAR.
C
    1 READ (1,1003) TITLE,ORG,ELECTR,DATE
      WRITE (Z,3001) TITLE
      WRITE (Z,3002)
      WRITE (Z,3003) GRAV,DHG,DH20
      WRITE (Z,3004) BOURD(1),BOURD(2)
```

```
      WRITE (Z,3005) CMICR,DIV,RADIUS
      WRITE (Z,3006) XL
      WRITE (Z,3007) IDATA,ICALIB,MSTART
      WRITE (Z,3008) ORG,ELECTR,DATE
C
C        TEST FOR TYPE OF DATA TO BE READ, READ POINTS,
C        CALCULATE Y.
C
      GO TO (2,8,14), IDATA
C
C        GAS PRESSURE WAS MEASURED WITH MANOMETER.
C
    2 WRITE (Z,3009)
      READ (1,1001) TCPHG,WATER,BOTCAP,CORR
      WRITE (Z,3010) TOPHG,WATER,BOTCAP,CORR
      DO 3 I=1,100
      READ (1,1001) VOLTS(I),MANTOP(I),MANBCT(I),DROPS(I)
      IF (VOLTS(I) + MANTOP(I) + MANBOT(I)) 3,4,3
    3 NPTS = I
    4 WRITE (Z,3011) (VCLTS(I),MANTOP(I),MANBOT(I),DROPS(I),
     1 I=1,NPTS)
      PRES = TOPHG - BOTCAP - DIV * CMICR - (WATER - BCTCAP -
     1 DIV * CMICR) * DH2O / DHG
      DO 5 I=1,NPTS
    5 Y(I) = PRES + MANTCP(I) - MANBCT(I) - CORR * DROPS(I)
C
      IF (ICALIB) 6,6,18
    6 CCNST = DHG * GRAV * RADIUS / 2.0
      DO 7 I=1,NPTS
    7 Y(I) = CCNST * Y(I)
      GO TO 17
C
C        GAS PRESSURE MEASURED WITH BOURDON GAUGE.
C
    8 WRITE (Z,3012)
      READ (1,1001) TCPHG,WATER,BOTCAP,CORR
      WRITE (Z,3010) TOPHG,WATER,BCTCAP,CORR
      DO 9 I=1,100
      READ (1,1001) VOLTS(I),DOD(I),DROPS(I)
      IF (VCLTS(I) + DOD(I)) 9,10,9
    9 NPTS = I
   10 WRITE (Z,3013) (VCLTS(I),DOD(I),DROPS(I), I=1,NPTS)
      PRES = TOPHG - BOTCAP - DIV * CMICR - (WATER - BOTCAP -
     1 DIV * CMICR) * DH2O / DHG
      DO 11 I=1,NPTS
      BCUR = BOURD(1) + BOURD(2) * COD(I)
   11 Y(I) = PRES + 2.540005 * BOUR * COD(I) - CORR * DROPS(I)
C
      IF (ICALIB) 12,12,18
   12 CCNST = DHG * GRAV * RADIUS / 2.0
```

```
      DO 13 I=1,NPTS
   13 Y(I) = CONST * Y(I)
      GO TO 17
C
C         DATA ALREADY IN DYNES/CM.
C
   14 WRITE (Z,3014)
      DO 15 I=1,100
      READ (1,1001) VOLTS(I),Y(I)
      IF (VOLTS(I) + Y(I)) 15,16,15
   15 NPTS = I
   16 WRITE (Z,3015) (VOLTS(I),Y(I), I=1,NPTS)
C
C         PUT TITLE FOR Y-AXIS INTO YL ARRAY.
C
   17 DO 171 I=1,5
  171 YL(I) = TYLG(I)
      GO TO 20
   18 DO 19 I=1,5
   19 YL(I) = TYLP(I)
C
C         PRINT TITLE FOR OUTPUT DATA, SET WEIGHTS = 1.0, PUT
C         TITLE INTO WTFACT ARRAY.
C
   20 WRITE (Z,3016) XL,YL
      DO 21 I=1,NPTS
   21 W(I) = 1.0
      DO 22 I=1,5
   22 WTFACT(I) = TWTF1(I)
C
C         FIT POLYNOMIAL TO DATA (VOLTS,Y), PRINT RESULTS.
C
      CALL FITECC
      WRITE (Z,3017) ORG,ELECTR,DATE,WTFACT
      WRITE (Z,3018) MDEG,RMS
      IF (VMAX + YMAX) 40,41,40
   41 WRITE (Z,3025)
      GO TO 42
   40 WRITE (Z,3024) VMAX, YMAX
   42 WRITE (Z,3019) (VOLTS(I),Y(I),YEST(I),ERROR(I),I=1,NPTS)
      WRITE (Z,3020)
C
C         CALCULATE WEIGHTS, PUT NEW TITLE INTO WTFACT ARRAY,
C         FIT NEW POLYNOMIAL TO DATA, PRINT INITIAL RESULTS.
C
      DO 23 I=1,NPTS
   23 W(I) = 0.3989423 * EXP ((ERROR(I)/WTRMS)**2 / (-2.))
      DO 24 I=1,5
   24 WTFACT(I) = TWTF2(I)
      CALL FITECC
```

```
      WRITE ($,3017) ORG,ELECTR,DATE,WTFACT
      WRITE ($,3018) MDEG,RMS
      IF (VMAX + YMAX) 43,44,43
   44 WRITE ($,3025)
      GO TO 45
   43 WRITE ($,3024) VMAX,YMAX
C
C         GRAPH CALCULATED E.C. CURVE AND DATA POINTS.
C
   45 VSIZE = AINT ((VOLTS(NPTS) - VOLTS(1)) / 0.2 + 2.0001)
      VO = VSIZE - 2.0
      DEG(1) = TDEG(MDEG)
      CALL GRAPH (NPTS,VOLTS,YEST,0,2,VSIZE,10.,0,0,0,0,XL,YL,
     1 GL,ORG)
      CALL GRAPH (NPTS,VOLTS,Y,1,7,0,0,0,0,0,0,0,0,0,0)
      CALL LETTER (VO,9.2,0.1,ELECTR,0.,20,0,0,0,0,0,0,0,0,0,
     1 0)
      CALL LETTER (VO,9.05,0.1,DATE,0.,20,0,0,0,0,0,0,0,0,0,0)
      CALL LETTER (VO,8.80,0.1,DEG,0.,20,0,0,0,0,0,0,0,0,0,0)
C
C         GRAPH REGION NEAR E.C. MAXIMUM.
C
      IF (VMAX + YMAX) 25,30,25
   25 YEXPO = AINT (YMAX - 9.0)
      J = 0
      DO 26 I=1,NPTS
      IF (Y(I) - YEXPO) 26,27,27
   27 J = J + 1
      VEXP(J) = VOLTS(I)
      YEXP(J) = Y(I)
      YESTEX(J) = YEST(I)
   26 CONTINUE
      VEXPSZ = AINT ((VEXP(J) - VEXP(1)) / 0.05 + 2.0001)
      VEO = VEXPSZ - 2.0
      CALL GRAPH (J,VEXP,YESTEX,0,2,VEXPSZ,10.,0,0,0,0,XL,YL,
     1 GL,ORG)
      CALL GRAPH (J,VEXP,YEXP,1,7,0,0,0,0,0,0,0,0,0,0)
      CALL LETTER (VEO,9.2,0.1,ELECTR,0.,20,0,0,0,0,0,0,0,0,0,
     1 0)
      CALL LETTER (VEO,9.05,0.1,DATE,0.,20,0,0,0,0,0,0,0,0,0,
     1 0)
      CALL LETTER (VEO,8.80,0.1,DEG,0.,20,0,0,0,0,0,0,0,0,0,0)
      CALL LETTER (VEO,8.65,0.1,SCALE,0.,20,0,0,0,0,0,0,0,0,0,
     1 0)
C
   30 IF (ICALIB) 31,31,34
C
C         FIND CHARGE AND CAPACITANCE.
C
   31 QCCF(MDEG) = -0.1 * CYCOF(MDEG)
```

```
      MDEG1 = MDEG - 1
      DC 32 J=1,MDEG1
      QCOF(J) = -0.1 * CYCCF(J)
   32 CCOF(J) = -0.1 * DDYCOF(J)
      DO 33 I=1,NPTS
      CALL PVAL (Q(I),VOLTS(I),QCCF,MDEG)
   33 CALL PVAL (C(I),VCLTS(I),CCOF,MDEG1)
C
C         PRINT FINAL RESULTS, GRAPH Q AND C.
C
      WRITE ($,3021) (VCLTS(I),W(I),Y(I),YEST(I),ERROR(I),
     1 Q(I),C(I), I=1,NPTS)
      CALL GRAPH (NPTS,VOLTS,Q,0,2,VSIZE,10.,0,0,C,0,XL,YLQ,
     1 GLQ,ORG)
      CALL LETTER (V0,9.2,0.1,ELECTR,0.,20,C,0,0,0,0,0,0,0,0,
     1 0)
      CALL GRAPH (NPTS,VOLTS,C,0,2,VSIZE,10.,0,0,0,0,XL,YLC,
     1 GLC,ORG)
      CALL LETTER (V0,9.2,0.1,ELECTR,0.,20,C,0,0,0,0,0,0,0,0,
     1 0)
C
C         PUNCH DATA CARCS FOR NEXT PROGRAM.
C
      MDEG1 = MDEG + 1
      WRITE (2,2001) GL,ORG,ELECTR
      WRITE (2,2002) (YCCF(J), J=1,MCEG1)
      GO TO 35
C
C         CALCULATE RADILS, PRINT FINAL RESULTS.
C
   34 RADIUS = (2.0 * RACIUS) / (YMAX * DHG * GRAV)
      WRITE ($,3022) RACIUS
      WRITE ($,3023) (VCLTS(I),W(I),Y(I),YEST(I),ERROR(I),
     1 I=1,NPTS)
C
C         TEST TC SEE IF LAST CATA SET.
C
   35 READ (1,1004) NDATA
      IF (NCATA) 1,36,1
   36 STOP
      END



      SUBROUTINE FITECC
C
C         PURPOSE
C           FITS THE DATA PCINTS WITH POLYNOMIALS FROM DEGREE 3
C           TO 10, FINDS THE RMS DEVIATION OF THE POINTS FROM
C           EACH FITTED POLYNOMIAL AND THE 1ST AND 2ND
```

```
C          DERIVATIVES AND THEIR ROOTS (BOTH REAL AND COMPLEX)
C          FOR EACH POLYNOMIAL.  THE "BEST FIT" (THE
C          POLYNOMIAL OF HIGHEST DEGREE WHICH HAS NO POINT OF
C          INFLECTION IN THE REGION OF THE DATA) IS FOUND.
C
C        NOTE - (1) IF IER>0 WHEN FINDING THE ROOTS OF THE
C          SECOND DERIVATIVE OF A POLYNOMIAL (SEE SUBROUTINE
C          POLRT FOR A DEFINITION OF IER), THE GIVEN
C          POLYNOMIAL IS PRESUMED TO HAVE A POINT OF
C          INFLECTION.
C               (2) IF ALL POLYNOMIALS HAVE A POINT OF
C          INFLECTION IN THE REGION OF THE DATA, THEN THE
C          POLYNOMIAL OF DEGREE 10 IS PRESUMED TO BE THE
C          "BEST FIT".
C
C        OTHER SUBROUTINES REQUIRED
C          CPLSPA
C          PDER
C          PVAL
C          POLRT
C          CPXCRD
C          PCLA
C
C
      COMMON  N, X(100), Y(100), W(100), COF(11), DCOF(10),
     1        DDCOF(9), RMS, WTRMS, XMAX, YMAX, MDEG,
     2        YEST(100), ERROR(100), CRG(5), ELECTR(5),
     3        WTFACT(5), DATE(5), MSTART, Z
      DIMENSION  COF1(11), YEST1(100), ERROR1(100), XMAX1(9),
     1           YMAX1(9), XMAXR(9), XMAXI(9), XFLX(8),
     2           YFLX(8), XFLXR(8), XFLXI(8)
      DOUBLE PRECISION  COFD(11), DCOFD(10), DDCOFD(9),
     1                  WCOF(10), ROOTR(9), ROOTI(9)
      INTEGER Z
      EQUIVALENCE  (XMAXR,XFLXR), (XMAXI,XFLXI)
C
C
 2001 FORMAT (/' POLYNOMIALS FIT TO DATA (VOLTS,Y) FOR ',5A4/
     1 2X,5A4,1X,5A4)
 2002 FORMAT (1X,5A4)
 2003 FORMAT (///'  POLYNOMIAL OF DEGREE ',I2/3X,
     1 'COEFFICIENTS, IN ORDER OF ASCENDING POWER OF VOLTS '/
     2 10X,'POLYNOMIAL',11X,'1ST DERIV',12X,'2ND DERIV')
 2004 FORMAT ( 1P3E21.7)
 2005 FORMAT (/'   RMS DEVIATION =',F6.3,9X,'WEIGHTED RMS',
     1 ' DEVIATION =',F6.3)
 2006 FORMAT (/'   EXTREMA')
 2007 FORMAT (5X,'REAL ROOTS'/9X,'VOLTS',8X,'Y-ESTIMATE')
 2008 FORMAT (F14.4,F16.3)
 2009 FORMAT ( 1P2E21.7/ E21.7)
```

```
 2010 FORMAT (5X,'THERE ARE NO REAL ROCTS')
 2011 FORMAT (/'   INFLECTICN POINTS')
 2012 FORMAT (/5X,'ERROR IN POLRT SUBRCUTINE, IER =',I2)
 2028 FORMAT (5X,'THERE ARE NO COMPLEX ROOTS')
 2029 FCRMAT (5X,'COMPLEX ROOTS')
 2030 FORMAT ( 1PE20.6,E16.6,' * I')
 2031 FCRMAT (///' ALL POLYNOMIALS HAVE POINTS OF INFLECTION'
     1 //' BEST FIT TO CATA IS ASSUMED TO BE PCLYNCMIAL OF',
     2 ' DEGREE 10.')
C
C
C          PRINT TITLES FCR INFORMATICN TO BE FOUND
C
      WRITE (Z,2001) ORG,ELECTR,DATE
      WRITE (Z,2002) WTFACT
      TUWYLC = 0.0
      IERFIT = 1
      M = MSTART
C
C          FIT DATA POINTS WITH LEAST SQUARES PCLYNCMIAL
C
    1 CALL CPLSPA (M,N,X,Y,W, COFD,TUWYLC)
      TUWYLO = 1.0
      MP1 = M + 1
      MM2 = M - 2
      DC 6 J = 1,MP1
    6 COF1(J) = SNGL(COFD(J))
C
C          FIND CERIVATIVES OF POLYNCMIAL AND PRINT RESULTS
C
      CALL PDER (DCCFD,M,COFD,MP1)
      CALL PCER (DDCOFD,MM1,DCOFD,M)
      WRITE (Z,2003) M
      WRITE (Z,2004) (CCFD(J),DCOFD(J),CCCOFD(J), J=1,MM1)
      WRITE (Z,2009) COFD(M),DCOFD(M),COFD(MP1)
C
C          FIND Y-ESTIMATES & ERRORS FOR EACH POINT AND FIND AND
C          PRINT RMS DEVIATICNS
C
      SUMW = 0.0
      SUMSQ = C.0
      SUMSQW = 0.0
      DC 7 I = 1,N
      CALL PVAL (YEST1(I),X(I),COF1,MP1)
      ERROR1(I) = YEST1(I) - Y(I)
      SUMW = SUMW + W(I)
      SUMSQ = SUMSQ + ERROR1(I) ** 2
      SUMSQW = SUMSQW + W(I) * ERROR1(I) ** 2
    7 CONTINUE
      WTRMS1 = SQRT (SUMSQW/ SUMW)
```

```
      RMS1 = SQRT (SUMSQ / FLCAT(N))
      WRITE (Z,2005) RMS1,WTRMS1
C
C         FIND THE ROOTS OF THE 1ST CERIVATIVE, PUT THE REAL
C         ROOTS IN ORDER & FIND THEIR Y-ESTIMATES.
C
      CALL POLRT (DCOFD,WCCF,MM1,ROCTR,ROOTI,IER)
      CALL CPXCRD (MM1,ROOTR,ROOTI,NRMAX ,XMAX1,NCMAX,XMAXR,
     1 XMAXI)
      DO 5 J = 1,NRMAX
    5 CALL PVAL (YMAX1(J),XMAX1(J),COF1,MP1)
C
C         PRINT RESULTANT EXTREMA
C
      WRITE (Z,2006)
      IF (IER) 101,101,102
  102 WRITE (Z,2012) IER
  101 IF(NRMAX ) 15,15,14
   15 WRITE (Z,2010)
      GO TO 103
   14 WRITE (Z,2007)
      WRITE (Z,2008) (XMAX1(J),YMAX1(J), J=1,NRMAX)
  103 IF (NCMAX) 104,104,105
  104 WRITE (Z,2028)
      GO TC 17
  105 WRITE (Z,2029)
      WRITE (Z,2030) (XMAXR(J),XMAXI(J), J=1,NCMAX)
C
C         FINC THE ROOTS CF THE 2ND CERIVATIVE, PUT THE REAL
C         RCOTS IN ORDER & FIND THEIR Y-ESTIMATES.
C
   17 CALL PCLRT (DDCOFC,WCOF,MM2,RCCTR,ROOTI,IER)
      CALL CPXORD (MM2,ROOTR,ROOTI,NRFLX,XFLX,NCFLX,XFLXR,
     1 XFLXI)
      DO 13 J = 1,NRFLX
   13 CALL PVAL (YFLX(J),XFLX(J),COF1,MP1)
C
C         PRINT RESULTANT INFLECTICN PCINTS
C
      WRITE (Z,2011)
      IF (IER) 106,106,107
  107 WRITE (Z,2012) IER
  106 IF (NRFLX) 19,19,20
   19 WRITE (Z,2010)
      GC TC 16
   20 WRITE (Z,2007)
      WRITE (Z,2008) (XFLX(J),YFLX(J), J=1,NRFLX)
   16 IF (NCFLX) 108,108,109
  108 WRITE (Z,2028)
      GO TO 18
```

```
  109 WRITE (Z,2029)
      WRITE (Z,2030) (XFLXR(J),XFLXI(J), J=1,NCFLX)
   18 IF (IER) 26,26,122
C
C          IF NO POINTS OF INFLECTION IN REGION OF DATA, STORE
C          YEST, ERROR, COF, DCOF, DCCOF, RMS, WTRMS.
C
   26 IF(NRFLX) 9,9,753
  753 DO 22 J = 1,NRFLX
      IF (X(1) - XFLX(J)) 21,22,22
   21 IF (XFLX(J) - X(N)) 122,22,22
   22 CONTINUE
    9 IERFIT = 0
      MDEG = M
      CALL PCLA (YEST,N,YEST1,N)
      CALL PCLA (ERROR,N,ERROR1,N)
      CALL PCLA (COF,MP1,CCF1,MP1)
      DO 13C J = 1,MM1
      DCOF(J) = SNGL(DCOFD(J))
  130 DDCOF(J) = SNGL(DCCOFO(J))
      DCOF(M) = SNGL(DCCFD(M))
      RMS = RMS1
      WTRMS = WTRMS1
C
C          FIND WHICH MAXIMUM POINT IS IN THE REGION OF THE DATA
C
      DO 4 J = 1,NRMAX
      K = J
      IF (X(1) - XMAX1(J)) 8,4,4
    8 IF (XMAX1(J) - X(N)) 10,4,4
    4 CCNTINUE
      XMAX = 0.0
      YMAX = 0.0
      GO TO 122
   10 XMAX = XMAX1(K)
      YMAX = YMAX1(K)
  122 IF (M-10) 121,120,120
  121 M = M + 1
      GO TC 1
C
C          IF ALL POLYNOMIALS HAVE POINTS OF INFLECTION, ASSUME
C          THE HIGHEST DEGREE POLYNOMIAL IS THE BEST FIT.
C
  120 IF (IERFIT) 2,2,3
    3 WRITE (Z,2031)
      GO TC 9
C
    2 RETURN
      END
```

```
      SUBROUTINE CPXORD (NIN,CRIN,CIIN,NROUT,RROUT,NCOUT,
     1                   CROUT,CIOUT)
C
      DIMENSION RROUT(10), CROUT(10), CIOUT(10)
      DOUBLE PRECISION CRIN(10), CIIN(10)
C
C
C        SEPARATE INPUT COMPLEX NUMBERS (CRIN + CIIN * I) INTO
C        PURE REAL NUMBERS (RROUT) AND COMPLEX NUMBERS (CROUT
C        + CIOUT * I).
C
      NROUT = 0
      NCOUT = 0
      DO 1 I = 1,NIN
      IF (CIIN(I)) 2,3,2
    3 NROUT = NROUT + 1
      RROUT(NROUT) = SNGL(CRIN(I))
      GO TO 1
    2 NCOUT = NCOUT + 1
      CROUT(NCOUT) = SNGL(CRIN(I))
      CIOUT(NCOUT) = SNGL(CIIN(I))
    1 CONTINUE
C
C        PUT PURE REAL NUMBERS IN ORDER FROM SMALLEST TO
C        LARGEST.
C
      M = NROUT - 1
      IF (M) 4,4,5
    5 DO 6 I = 1,M
      K = I + 1
      DO 6 J = K,NROUT
      IF (RROUT(I) - RROUT(J)) 6,6,7
    7 X = RROUT(I)
      RROUT(I) = RROUT(J)
      RROUT(J) = X
    6 CONTINUE
C
    4 RETURN
      END
```

```
C         SECOND PROGRAM FOR ANALYSIS OF ELECTROCAPILLARY DATA
C
C
C
      CCMMON  NCONCS, NVOLTS, VSTART, VINC, MBASE, BBASE,
     1        M, B, CONC, ACT, LNACT, VOLTS, YBASE, Y, PI
      DIMENSION  TITLE(40), ORG(5), ELECTR(5), NAME(5),
     1           ABASE(11), M(10), CONC(10), A(11,10),
     2           BBASE(11), LNACT(10), B(11,10), VCLTS(40),
     3           YBASE(40), Y(40,10), PI(10,40), ACT(10)
      REAL  NAME, LNACT
C
 1001 FORMAT (20A4/20A4)
 1002 FORMAT ('1'////1X,20A4/2X,20A4)
 1003 FORMAT (//'  INPUT PARAMETERS'//4X,'ORG',20X,'ELECTR',
     1 17X,'NAME'/4X,5A4,3X,5A4,3X,5A4)
 1004 FORMAT (2I10,4F10.0)
 1005 FORMAT (/4X,'NCONCS',4X,'NVOLTS',4X,'VSTART',6X,'VINC',
     1 6X,'VECM',8X,'CO')
 1006 FORMAT (I10,F10.C)
 1C07 FORMAT (//'  INPUT COEFFICIENTS FOR PCLYNOMIALS')
 1008 FORMAT (1P4E15.7)
 1009 FORMAT (/3X,'CONCN',6X,'0.0',3X,10F10.6)
 1010 FORMAT (3X,'DEGREE',I8,10I10/)
 1011 FCRMAT (I6,3X,11F1C.2)
 1012 FORMAT (//'  COEFFICIENTS OF TRANSFORMED PCLYNOMIALS'/
     1 '   (NOW IN TERMS OF VOLTS VS. ELECTROCAPILLARY',
     2 ' MAXIMUM OF '/'   BASE ELECTRCLYTE)')
 1013 FORMAT (2I10,3F10.3,F10.4)
C
C         INITIALIZE ALL POLYNOMIAL COEFFICIENTS TO ZERO.
C
      DO 7 I=1,11
      ABASE(I) = 0.0
      BBASE(I) = 0.0
      DO 7 J=1,10
      A(I,J) = 0.0
    7 B(I,J) = 0.0
C
C         READ IN & WRITE OUT DATA
C
    4 READ (1,1001) TITLE
      WRITE (3,1002) TITLE
      READ (1,1001) ORG,ELECTR,NAME
      WRITE (3,1003) ORG,ELECTR,NAME
      READ (1,1004) NCONCS,NVOLTS,VSTART,VINC,VECM,CO
      WRITE (3,1005)
      WRITE (3,1013) NCCNCS,NVOLTS,VSTART,VINC,VECM,CO
      READ (1,1006) MBASE
      MP1 = MBASE + 1
```

```
      READ (1,1008) (ABASE(I), I=1,MP1)
      DO 1 J=1,NCONCS
      READ (1,1006) M(J),CONC(J)
      MP1 = M(J) + 1
    1 READ (1,1008) (A(I,J),I=1,MP1)
      WRITE (3,1007)
      WRITE (3,1009) (CONC(J), J=1,NCONCS)
      WRITE (3,1010) MBASE,(M(J), J=1,NCONCS)
      DO 5 I=1,11
      K = I - 1
    5 WRITE (3,1011) K,ABASE(I),(A(I,J), J=1,NCONCS)
C
C         TRANSFORM POLYNOMIALS TO VOLTS VS. E.C.MAX.
C
      CALL SHIFT (MBASE,VECM,ABASE,BBASE)
      DO 2  J=1,NCONCS
      ACT(J) = CONC(J) / CO
      LNACT(J) = ALOG (ACT(J))
    2 CALL SHIFT (M(J),VECM,A(1,J),B(1,J))
      WRITE (3,1012)
      WRITE (3,1009) (CONC(J), J=1,NCONCS)
      WRITE (3,1010) MBASE,(M(J), J=1,NCONCS)
      DO 6  I=1,11
      K = I - 1
    6 WRITE (3,1011) K,BBASE(I),(B(I,J), J=1,NCONCS)
C
C
      CALL FINDPI
C
C
      CALL COMBIN (NCONCS,NVOLTS,VOLTS,YBASE,Y,ORG,ELECTR,
     1 NAME)
C
C
      READ (1,1006) NDATA
      IF (NDATA) 4,3,4
    3 STOP
      END



      SUBROUTINE SHIFT (M,X,A,B)
C
C        PURPOSE
C           TRANSFORMS THE EQUATION OF A POLYNOMIAL WHEN THE
C           ORIGIN IS SHIFTED TO A NEW POSITION (X,0) ALONG THE
C           X-AXIS.
C
C        DESCRIPTION OF PARAMETERS
C           M = DEGREE OF POLYNOMIAL
```

```
C          X = X-VALUE (IN OLD COORDINATE SYSTEM) OF NEW
C              ORIGIN
C          A = ARRAY OF COEFFICIENTS OF OLD POLYNOMIAL,
C              ORDERED FROM SMALLEST TO LARGEST POWER
C          B = ARRAY OF COEFFICIENTS OF NEW POLYNOMIAL
C
C
      DIMENSION A(11),B(11)
C
      MP1 = M + 1
      B(1) = 0.
      DO 3 I = 1,MP1
    3 B(1) = B(1) + A(I) * X**(I-1)
C
      DO 2 J = 2,MP1
      JM1 = J - 1
      B(J) = 0.
      DO 2 I = J,MP1
      U = 1.
      DO 1 K = 1,JM1
    1 U = U * (FLOAT(I-K) / FLOAT(K))
    2 B(J) = B(J) + U * A(I) * X**(I-J)
C
      RETURN
      END



      SUBROUTINE FINDPI
C
C        PURPOSE
C          FINDS VALUES OF THE INTERFACIAL TENSION (Y) AND OF
C          THE SPREADING PRESSURE (PI) AS A FUNCTION OF
C          POTENTIAL AND CONCENTRATION OF ORGANIC SOLUTE AND
C          PRINTS THESE VALUES IN TWO TABLES.
C
C        OTHER SUBROUTINES REQUIRED
C          PVAL
C
C
      COMMON  NCONCS, NVOLTS, VSTART, VINC, MBASE, BBASE,
     1        M, B, CONC, ACT, LNACT, VOLTS, YBASE, Y, PI
      DIMENSION  BBASE(11), M(10), B(11,10), CONC(10),
     1           LNACT(10), VOLTS(40), YBASE(40), Y(40,10),
     2           PI(10,40), VL(3), ACT(10)
      REAL  LNACT
C
 1001 FORMAT ('1'////'  INTERFACIAL TENSION (Y)'//
     1 '   SOLUTION',12X,'BASE',I9,9I10)
 1002 FORMAT ('   CONCENTRATION',13X,10F10.6)
```

```
 1003 FORMAT ('   LN(C/CO)',18X,10F10.4)
 1004 FORMAT (13X,'VOLTS')
 1005 FORMAT (F18.3,11F10.2)
 1006 FORMAT ('1'////'  SPREADING PRESSURE (PI)'//
     1 '   SOLUTION',5X,10I10)
 1007 FORMAT ('   CCNCENTRATION',3X,10F1C.6)
 1008 FORMAT ('   LN(C/CO)',8X,10F1C.4)
 1009 FORMAT (8F10.4)
 101C FORMAT (8F10.2)
 1011 FCRMAT ('   ACTIVITY (C/CO)',11X,10F1C.6)
 1C12 FORMAT ('   ACTIVITY (C/CO) ',10F10.6)
 1013 FCRMAT (F6.3,2X,3A4)
C
      DATA VL/12HVOLTS VS ECM/
C
      MP1 = MBASE + 1
      DO 1 K=1,NVOLTS
      REALK = FLOAT (K-1)
      VCLTS(K) = VSTART + REALK * VINC
    1 CALL PVAL (YBASE(K),VOLTS(K),BBASE,MP1)
C
      DC 2 J=1,NCONCS
      MP1 = M(J) + 1
      DO 2 K=1,NVOLTS
      CALL PVAL (Y(K,J),VOLTS(K),B(1,J),MP1)
    2 PI(J,K) = YBASE(K) - Y(K,J)
C
      WRITE (3,1001) (J, J=1,NCONCS)
      WRITE (3,1002) (CCNC(J), J=1,NCONCS)
      WRITE (3,1011) (ACT(J), J=1,NCONCS)
      WRITE (3,1003) (LNACT(J), J=1,NCCNCS)
      WRITE (3,1004)
C
      DO 3 K=1,NVOLTS
      WRITE (3,1005) VOLTS(K),YBASE(K),(Y(K,J), J=1,NCONCS)
    3 CONTINUE
C
      WRITE (3,1006) (J, J=1,NCONCS)
      WRITE (3,1007) (CONC(J), J=1,NCONCS)
      WRITE (3,1012) (ACT(J), J=1,NCONCS)
      WRITE (3,1008) (LNACT(J), J=1,NCCNCS)
      WRITE (3,1004)
C
      DO 4 K=1,NVOLTS
    4 WRITE (3,1005) VOLTS(K),(PI(J,K), J=1,NCONCS)
C
      WRITE (2,1009) (LNACT(J), J=1,NCCNCS)
      DO 5 K=1,NVOLTS
      WRITE (2,1013) VOLTS(K),VL
    5 WRITE (2,101C) (PI(J,K), J=1,NCONCS)
```

```
C
C
      RETURN
      END


      SUBROUTINE COMBIN (NCONCS,NVOLTS,VOLTS,YBASE,Y,ORG,
     1 ELECTR,NAME)
C
C         PURPOSE
C            GRAPHS ELECTRCCAPILLARY CURVES FOR PURE ELECTROLYTE
C            AND FCR ALL CONCENTRATICNS CF ORGANIC SOLUTE ON THE
C            SAME GRAPH.
C
      DIMENSION  VOLTS(40), YBASE(40), Y(40,10), ORG(5),
     1           ELECTR(5), NAME(5), XL(5), YL(5), GL(5),
     2           DL(5), LABL(7)
      REAL  NAME , LABL
C
      DATA XL  /20HVOLTS VS. E.C. MAX. /,
     1     YL  /20HGAMMA (DYNES/CM)    /,
     2     GL  /20H                    /,
     3     DL  /20H                    /,
     4     LABL/28HELECTROCAPILLARY CURVES FOR /
C
      CALL ORIGIN (1.0,1.5,1)
      CALL GRAPH (NVOLTS,VOLTS,YBASE,0,2,4.0,5.5,0.4,-0.8,
     1 20.0,320.0,XL,YL,GL,DL)
      DO 1 J=1,NCONCS
    1 CALL GRAPH (NVOLTS,VCLTS,Y(1,J),0,2,0,0,0,0,0,0,0,0,0,0)
      CALL LETTER (0.0,-1.0,0.15,LABL,0.0,28,0,0,0,0,0,0,0,0,
     1 0,0)
      CALL LETTER (3.6,-1.0,0.15,ORG,0.0,20,0,0,0,0,0,0,0,0,0,
     1 0)
      CALL LETTER (0.0,-1.25,0.15,ELECTR,0.C,20,0,0,0,0,0,0,0,
     1 0,0,0)
      CALL LETTER (3.0,-1.25,0.15,NAME,0.0,20,0,0,0,0,C,0,0,0,
     1 C,0)
      CALL ORIGIN (7.0,0.0,0)
C
      RETURN
      END
```

```
C         PROGRAM FOR FITTING FRUMKIN EQUATION TO ELECTRO-
C         CAPILLARY DATA FROM A COMPOSITE PI VS. LN ACT CURVE
C
C
      REAL*4  ORG(5), ELECTR(5), NAME(5), LNAL(5), PIL(5),
     1        THL(5), REDAL(5), VL(5), F0L(5), F1L(5),
     2        GL1(5), GL2(5), GL3(5), GL4(5),
     3        LNA(100), PI(100),          G(50), TH(50),
     4        X(50), Y(50), TH$(21), LNA$(21), PI$(21),
     5        REDA$(21), V(50), F0(50), F1(50),
     6        LNA1, LNA2, LNAC, LNAINC, LAHAF
      INTEGER OUT
      EQUIVALENCE  (LNA,V), (PI,TH$,F0),   (LNA$,F1),
     1             (G,PI$), (X,REDA$)
C
C
 1001 FORMAT (20A4)
 1002 FORMAT (I10,F10.0)
 1003 FORMAT (8F10.0)
 1004 FORMAT (2F10.0)
 1005 FORMAT (2I10)
C
 2001 FORMAT ('1'////' FRUMKIN EQUATION FIT TO ELECTRO',
     1 'CAPILLARY DATA FOR'/2X,5A4,1X,5A4,1X,5A4/'  ABSCISSA'
     2 ' OF COMPOSITE PI VS. LN A CURVE IS ',5A4)
 2002 FORMAT (/'  THETA(',I2,') = ',F5.3)
 2003 FORMAT (/'  MAXIMUM SURFACE EXCESS = ',F5.3,'X10**(-10'
     1 ,') MOLES/CM**2'/'  ACTIVITY FOR HALF COVERAGE = ',
     2 1PE9.3/'  ALPHA = ',0PF7.4/'  B-ZERO = ',1PE9.3/
     3 '  E-ZERO-PRIME = ',0PF6.4/'  EQUATION FOR ISOTHERM  ',
     4 'LN(TH/(A*(1-TH))) = (',F7.4,')*TH + (',F6.3,')'/
     5 '  EQUATION OF STATE  PI = (',F7.3,')*TH**2 + (',F6.2,
     6 ')*LN(1-TH)')
 2004 FORMAT (/'  SURFACE',4X,'THETA',5X,'LN A',6X,'LN A',8X,
     1 'A',6X,'A/AHALF',5X,'PI',8X,'PI'/3X,'EXCESS',13X,
     2 '(EXPTL)',3(3X,'(CALCD)'),3X,'(EXPTL)',3X,'(CALCD)')
 2005 FORMAT (F8.2,F10.3,2F10.2,F11.4,F9.2,2F10.1)
 2006 FORMAT ('1'////' FREE ENERGIES OF ADSORPTION FOR'/2X,
     1 5A4,1X,5A4,1X,5A4/'  POTENTIAL IS IN UNITS OF ',5A4//
     2 ' POTENTIAL',2X,'LNAINC',4X,'LN AHALF',3X,'F(00)',5X,
     3 'F(01)')
 2007 FORMAT (2F9.3,3F10.2)
C
C
C        PUT ALPHANUMERIC DATA INTO ARRAYS FOR GRAPH LABELS.
C
      DATA  PIL   /20HPI (DYNES/CM)        /,
     1      THL   /20HTHETA                /,
     2      REDAL /20HA/AHALF              /,
     3      F0L   /20H-F(00) (KCAL/MOLE)   /,
```

```
     4      FI1   /20H-F(0I) (KCAL/MOLE)  /,
     5      GL1   /20HLS FIT TO FRUMKIN EQ/,
     6      GL2   /20HCOMPOSITE CURVE FOR /,
     7      GL3   /20HDIMENSIONLESS ISOTH./,
     8      GL4   /20HFREE ENERGY OF ADS. /
C
      IN = 1
      OUT = 3
   12 READ (IN,1001) ORG,ELECTR,NAME,LNAL
      WRITE (OUT,2001) ORG,ELECTR,NAME,LNAL
      READ (IN,1005) NCPT,MCPT
      IF (MCPT.EQ.1) GO TO 13
      READ (IN,1004) GMAX
      GO TO 14
C
C         CALCULATE GAMMA-MAX FROM POINTS ON MONOLAYER PORTION
C         OF COMPOSITE CURVE (READ IN ACTUAL DATA POINTS).
C
   13 READ (IN,1002) N
      READ (IN,1004) (LNA(I),PI(I), I=1,N)
      CALL FOLSPA (N,LNA,PI,A,B)
      GMAX = B / 2.4789
C
C         CALCULATE GAMMA, THETA, AND Y FROM SLOPES OF
C         TANGENTS TO COMPOSITE CURVE (READ IN POINTS FROM
C         HAND DRAWN TANGENTS & FROM HAND FIT TO CURVE).
C
   14 READ (IN,1002) M
      N = 1
      DO 2 I=1,M
      READ (IN,1003) LNA1, PI1, LNA2, PI2, LNA(I), PI(I)
      G(N) = (PI2 - PI1) / (2.4789 * (LNA2 - LNA1))
      TH(N) = G(N) / GMAX
      IF (TH(N) - 1.0) 7,8,8
    8 WRITE (OUT,2002) I,TH(N)
      GO TO 2
    7 X(N) = ALOG (TH(N) / (1.0 - TH(N)))
      Y(N) = X(N) - LNA(N)
      N = N + 1
    2 CONTINUE
      N = N - 1
C
C         FIT LN A VS. THETA WITH FRUMKIN EQUATION.
C
      IF (NCPT.EQ.1) GO TO 9
      READ (IN,1004) A,B
      GO TO 10
    9 CALL FOLSPA (N,TH,Y,B,A)
   10 BZERO = EXP(B)
      ALPHA = A / 2.0
```

```
      D = -2.4789 * GMAX
      C = ALPHA * D
      AHALF = EXP (-1.0 * (0.5 * A + B))
      BZP = AHALF * BZERO
      WRITE (OUT,2003) GMAX,AHALF,ALPHA,BZERO,BZP,A,B,C,D
C
C        CALCULATE THEORETICAL LN A AND PI.
C
      WRITE (OUT,2004)
      DO 3 I=1,N
      LNAC = X(I) - A * TH(I) - B
      PIC = C * TH(I) * TH(I) + D * ALOG (1.0 - TH(I))
      AC = EXP (LNAC)
      REDAC = AC / AHALF
    3 WRITE (OUT,2005) G(I),TH(I),LNA(I),LNAC,AC,REDAC,PI(I),
     1 PIC
C
C        CALCULATE POINTS FOR THEORETICAL CURVES.
C
      TH$(1) = 0.025
      TH$(2) = 0.05
      TH$(21) = 0.975
      DO 4 I=3,20
    4 TH$(I) = TH$(I-1) + 0.05
      DO 5 I=1,21
      LNA$(I) = ALOG (TH$(I) / (1.0 - TH$(I))) - A * TH$(I)
     1 - B
      PI$(I) = C * TH$(I) * TH$(I) + D * ALOG (1.0 - TH$(I))
    5 REDA$(I) = EXP (LNA$(I)) / AHALF
C
      CALL GRAPH (N,TH,LNA,1,7,12.0,8.0,0.1,0.0,0.0,THL,LNAL,
     1 GL1,ORG)
      CALL GRAPH (21,TH$,LNA$,0,2,0,0,0,0,0,0,0,0,0,0)
      CALL LETTER (10.0,7.2,0.1,ELECTR,0.,20,0,0,0,0,0,0,0,0,
     1 0,0)
      CALL LETTER (10.0,7.05,0.1,NAME,0.,20,0,0,0,0,0,0,0,0,
     1 0,0)
      READ (IN,1003) XSIZE,XSF,XMIN,YSF,YMIN
C        THESE PARAMETERS SHOULD BE THE SAME AS FOR EC4.
      CALL GRAPH (21,LNA$,PI$,0,2,XSIZE,10.0,XSF,XMIN,YSF,
     1 YMIN,LNAL,PIL,GL2,ORG)
      XC = XSIZE -2.0
      CALL LETTER (XC,9.2,0.1,ELECTR,0.,20,0,0,0,0,0,0,0,0,0,
     1 0)
      CALL LETTER (XC,9.05,0.1,NAME,0.,20,0,0,0,0,0,0,0,0,0,
     1 0)
      IF (NCPT.EQ.1) GO TO 11
      CALL GRAPH (21,REDA$,TH$,0,2,10.0,8.0,1.0,0.0,0.2,0.0,
     1 REDAL,THL,GL3,ORG)
      CALL LETTER (6.0,7.2,0.1,ELECTR,0.,20,0,0,0,0,0,0,0,0,
```

```
     1 0,0)
      CALL LETTER (8.0,7.05,0.1,NAME,0.,20,0,0,0,0,0,0,0,0,0,
     1 0)
C
C        FIND FREE ENERGIES.
C
      READ (IN,1002) N,CO
      READ (IN,1001) VL
      WRITE (OUT,2006) ORG,ELECTR,NAME,VL
      T = ALOG (AHALF)
      U1 = -1.0 * (T + B + ALOG (55.5 / CO))
      U2 = -1.0 * (T + B + A)
      DO 6 I=1,N
      READ (IN,1003) V(I),LNAINC
      LAHAF = LNAINC + T
      F0(I) = 0.5923 * (U1 + LAHAF)
      F1(I) = 0.5923 * (U2 + LAHAF)
      WRITE (OUT,2007) V(I),LNAINC,LAHAF,F0(I),F1(I)
      F0(I) = -1.0 * F0(I)
    6 F1(I) = -1.0 * F1(I)
C
      CALL GRAPH (N,V,F0,1,11,8.0,10.0,0.2,-0.8,0.4,2.0,
     1 VL,F0L,GL4,ORG)
      CALL LETTER (6.0,9.2,0.1,ELECTR,0.,20,0,0,0,0,0,0,0,0,0,
     1 0,0)
      CALL LETTER (6.0,9.05,0.1,NAME,0.,20,0,0,0,0,0,0,0,0,0,
     1 0)
      CALL GRAPH (N,V,F1,1,11,8.0,10.0,0.2,-0.8,0.4,0.8,
     1 VL,F1L,GL4,ORG)
      CALL LETTER (6.0,9.2,0.1,ELECTR,0.,20,0,0,0,0,0,0,0,0,0,
     1 0,0)
      CALL LETTER (6.0,9.05,0.1,NAME,0.,20,0,0,0,0,0,0,0,0,0,
     1 0)
   11 READ (IN,1002) NDATA
      IF (NDATA.GT.0) GO TO 12
      STOP
      END



      SUBROUTINE FDLSFA (N,X,Y,A,B)
      REAL*4  X(1),Y(1)
      REAL*8  SUMX,SUMY,SUMX2,SUMXY,XD,YD,ND,BD,AD
      SUMX = 0.0D0
      SUMY = 0.0D0
      SUMX2 = 0.0D0
      SUMXY = 0.0D0
      DO 1 I=1,N
      XD = DBLE(X(I))
      YD = DBLE(Y(I))
```

```
      SUMX = SUMX + XD
      SUMY = SUMY + YD
      SUMX2 = SUMX2 + XD*XD
    1 SUMXY = SUMXY + XD*YD
      ND = DFLOAT(N)
      BD = (ND * SUMXY - SUMY * SUMX) / (ND * SUMX2 - SUMX *
     1      SUMX)
      AD = (SUMY - BD * SUMX) / ND
      A = SNGL(AD)
      B = SNGL(BD)
      RETURN
      END
```

APPENDIX C

Output Data From Computer Programs

EC1	Sample of output data from program EC1. Corresponds to Figures 2-5 of Appendix A.	Page 118
EC2	The first page for each compound lists the coefficients of the polynomials fit to each electrocapillary curve by program EC1. The second page lists the interfacial tensions computed from the polynomials for various potentials and concentrations of adsorbate.	Page 119
EC5	Parameters of Frumkin equation fit to electrocapillary data for each compound. Tables of values of various surface variables.	Page 127

```
BEST FIT TO DATA FOR PURE                    C.1CC1N HCLO4        (7-9-68) #2
 WEIGHTS WERE USED

 PCLYNOMIAL OF DEGREE 1C WAS BEST FIT.
 RMS DEVIATION = 0.C22
 COORDINATES OF ELFCTROCAPILLARY MAXIMUM ARE (-0.479,425.602)

   VOLTS     WEIGHT      Y(EXPTL;     Y(CALCD)     ERROR       O        C
  -1.100     0.398       384.761      384.762      0.001    -11.55     3.72
  -1.050     0.398       390.444      390.441     -0.003    -11.09    13.31
  -1.000     0.395       395.802      395.800     -0.002    -1C.33    16.36
  -0.950     0.361       400.744      400.757      0.013     -9.50    16.51
  -0.900     0.311       405.314      405.302     -0.013     -8.69    15.92
  -C.85C     0.393       409.445      409.448      0.003     -7.90    15.73
  -0.800     0.396       413.204      413.199     -0.005     -7.10    16.36
  -C.750     0.392       416.546      416.539     -0.006     -6.25    17.79
  -0.700     C.347       419.424      419.434      C.010     -5.31    19.78
  -C.650     0.277       421.814      421.833      0.019     -4.27    21.97
  -C.600     0.329       423.694      423.684     -0.010     -3.12    24.03
  -0.550     0.283       424.948      424.935     -0.013     -1.87    25.69
  -C.500     0.333       425.551      425.544     -0.007     -0.56    26.80
  -0.450     0.252       425.458      425.485      0.026      0.80    27.29
  -0.400     0.216       424.762      424.745     -0.017      2.16    27.20
  -0.350     0.053       423.277      423.325      0.049      3.51    26.67
  -0.300     0.219       421.257      421.240     -0.017      4.83    25.87
  -0.250     0.139       418.472      418.508      0.036      6.10    24.98
  -0.200     0.151       415.177      415.151     -0.026      7.32    24.19
  -0.150     C.399       411.185      411.188      0.003      8.52    23.64
  -0.100     0.166       406.660      406.635     -0.025      9.69    23.41
  -C.050     0.171       401.463      401.495      0.032     1C.87    23.52
   0.0       0.244       395.779      395.766     -0.013     12.05    23.92
   C.050     0.C25       389.377      389.439      0.063     13.26    24.46
   0.100     0.186       382.512      382.501     -0.010     14.50    24.98
   0.150     0.397       374.929      374.939      0.01C     15.75    25.27
   0.2CC     0.230       366.767      366.746     -0.021     17.02    25.11
   0.250     0.184       357.912      357.926      0.014     18.25    24.33
   0.300     0.371       348.502      348.500     -0.002     19.44    22.81
```

```
*************************************************************************************************************

SECOND ANALYSIS OF ELECTROCAPILLARY DATA FOR 3-PENTANOL
 IN 0.100N HCLO4 - DATA OF C. BROADHEAD


 INPUT PARAMETERS

   ORG                          ELECTR                     NAME
   3-PENTANOL                   IN 0.100N HCLO4            DATA OF C. BROADHEAD

   NCONCS     NVOLTS     VSTART        VINC        VECM        C0
        7         26     -0.633       0.050      -0.478    0.5880


 INPUT COEFFICIENTS FOR POLYNOMIALS

  CONCN       0.0       0.004650   0.012160   0.024320   0.046230   0.092460   0.231140   0.462280
  DEGREE      10          10         10          6          9          8          9         10
    0        394.99     394.80     394.01     394.74     393.57     388.66     388.14     382.26
    1       -118.40    -118.56    -113.60    -113.53    -104.99     -81.37     -55.43     -41.01
    2       -104.72     -97.59     -89.18    -154.71    -149.05     -37.34    -227.65    -171.42
    3        -42.37     -24.16     -74.91      24.99      82.17     136.12    -424.71    -288.90
    4       -151.63    -226.74    -450.12      87.93     -40.40   -1595.53      28.21     -52.58
    5        159.48      20.65     297.26     -19.15    -649.56   -6566.57    2459.47     734.15
    6        547.45     708.56    2030.91     -41.80    -296.10   -9749.18    5885.81     914.49
    7         -0.97     382.20     578.10       0.0      861.89   -6521.52    6449.51    -326.49
    8       -759.76    -674.79   -3026.66       0.0      951.87   -1665.17    3470.15   -1370.06
    9       -519.66    -776.81   -3127.70       0.0      280.01       0.0      740.55    -968.84
   10       -152.57    -225.92    -904.98       0.0        0.0        0.0        0.0     -225.89


 COEFFICIENTS OF TRANSFORMED POLYNOMIALS
  (NOW IN TERMS OF VOLTS VS. ELECTROCAPILLARY MAXIMUM OF
  BASE ELECTROLYTE)

  CONCN       0.0       0.004650   0.012160   0.024320   0.046230   0.092460   0.231140   0.462280
  DEGREE      10          10         10          6          9          8          9         10
    0        425.56     424.72     421.38     415.50     408.61     401.14     391.03     383.34
    1         -0.07       3.20      11.93      14.34      21.68      20.90      17.90      16.93
    2       -142.06    -135.01    -116.06     -81.81     -35.95     -15.88     -29.84     -30.23
    3        -40.42     -75.00    -199.97     -95.59    -152.72    -128.87     -38.44      -6.67
    4        136.92     163.42      96.90      -9.56    -199.33    -432.53      21.43      48.74
    5        114.96     259.75     875.01     100.73     355.32     239.08     172.38     -28.16
    6       -297.67    -237.49    -494.06     -41.80     340.83    1452.26    -287.71    -346.33
    7       -193.11    -466.15   -1714.18       0.0     -474.88    -163.91    -728.97     -96.03
    8        337.36     344.20    1123.97       0.0     -252.72   -1665.17     284.29     475.33
    9        109.62     307.08    1198.07       0.0      280.01       0.0      740.55     110.92
   10       -152.57    -225.94    -904.97       0.0        0.0        0.0        0.0     -225.89
```

```
INTERFACIAL TENSION (Y)

SOLUTION             BASE        1          2          3          4          5          6          7
CONCENTRATION                0.004850   0.012160   0.024320   0.046230   0.092460   0.231140   0.462280
ACTIVITY (C/CO)              0.008249   0.020680   0.041361   0.078622   0.157245   0.393095   0.786190
LN(C/CO)                      -4.7977    -3.8786    -3.1854    -2.5431    -1.8500    -0.9337    -0.2406
             VOLTS
            -0.633  383.29     383.12     382.77     383.42     381.29     377.67     369.84     362.63
            -0.583  389.10     389.64     388.28     388.74     385.76     381.58     372.36     365.10
            -0.533  394.54     394.21     393.62     393.02     389.60     384.27     374.74     367.41
            -0.483  399.59     399.20     398.58     396.56     392.86     386.55     376.99     369.54
            -0.433  404.22     403.77     402.95     399.56     395.61     388.71     379.08     371.49
            -0.383  408.44     407.89     406.65     402.21     397.88     390.78     380.97     373.29
            -0.333  412.27     411.58     409.73     404.59     399.77     392.68     382.68     374.95
            -0.283  415.66     414.65     412.30     406.79     401.36     394.37     384.23     376.50
            -0.233  418.67     417.70     414.51     408.82     402.78     395.82     385.65     377.95
            -0.183  421.19     420.13     416.46     410.69     404.09     397.09     386.97     379.32
            -0.133  423.19     422.10     418.20     412.36     405.37     398.25     388.21     380.58
            -0.083  424.62     423.57     419.71     413.80     406.64     399.35     389.36     381.73
            -0.033  425.41     424.47     420.87     414.94     407.86     400.44     390.41     382.75
             0.017  425.52     424.74     421.55     415.72     408.97     401.49     391.32     383.62
             0.067  424.91     424.31     421.60     416.06     409.85     402.42     392.08     384.34
             0.117  423.57     423.15     420.90     415.90     410.38     403.09     392.66     384.90
             0.167  421.52     421.25     419.38     415.17     410.41     403.31     393.04     385.32
             0.217  418.77     418.61     417.01     413.80     409.81     402.91     393.20     385.58
             0.267  415.38     415.28     413.86     411.75     408.47     401.73     393.13     385.66
             0.317  411.40     411.31     410.00     408.96     406.30     399.71     392.77     385.52
             0.367  406.87     406.75     405.55     405.41     403.28     396.90     392.04     385.07
             0.417  401.83     401.67     400.62     401.08     399.40     393.44     390.77     384.19
             0.467  396.28     396.09     395.25     395.97     394.71     389.55     388.72     382.69
             0.517  390.21     390.02     389.44     390.07     389.25     385.44     385.61     380.38
             0.567  383.58     383.44     383.12     383.43     383.10     381.08     381.12     377.05
             0.617  376.35     376.28     376.16     376.06     376.27     375.98     375.08     372.49
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SECOND ANALYSIS OF ELECTROCAPILLARY DATA FOR CHLOROFORM
 IN 0.100N HCLO4 - DATA OF D. BROADHEAD


 INPUT PARAMETERS

   ORG                         ELECTR                     NAME
   CHLOROFORM                  IN 0.100N HCLO4            DATA OF D. BROADHEAD

   NCONCS     NVOLTS     VSTART       VINC       VECM         CO
        8         25     -0.600      0.050     -0.474     0.0494


 INPUT COEFFICIENTS FOR POLYNOMIALS

  CONCN         0.0     0.012580   0.017820   0.025130   0.031630   0.037690   0.044500   0.046000   0.049400
  DEGREE         10        10         10          9          9         10         10         10         10
    0        395.10     394.56     394.80     394.54     394.19     394.22     394.19     394.40     393.82
    1       -117.56    -118.08    -116.59    -116.00    -122.67    -118.53    -113.61    -113.70    -101.49
    2       -123.57    -100.67    -115.00    -101.73    -115.60    -132.02    -152.58    -216.85    -291.57
    3       -107.06      -1.74     -34.16       7.50     210.60     193.50      95.44     158.18     -79.29
    4        162.28    -199.12     -41.87    -356.25       2.67     -68.21     687.99    1272.62    2003.71
    5       1492.70    -198.11     340.64    -501.80   -1401.64   -1718.15     338.45     773.64    3568.81
    6        374.92     394.00     203.05    1244.21   -1595.40    -972.28   -2325.15   -5627.91   -5674.99
    7      -7021.84     727.98   -2009.79    3451.65     791.22    4745.39   -6317.46  -15559.37  -25276.71
    8     -12969.89     229.97   -4059.04    2873.52    1936.93    8215.44   -7831.92  -18187.77  -32596.39
    9      -9149.99    -192.19   -2965.17     818.13     750.76    5043.36   -4858.74  -10352.92  -18837.59
   10      -2346.91    -105.41    -771.98       0.0        0.0     1102.92   -1194.29   -2334.60   -4167.46


 COEFFICIENTS OF TRANSFORMED POLYNOMIALS
  (NOW IN TERMS OF VOLTS VS. ELECTROCAPILLARY MAXIMUM OF
  BASE ELECTROLYTE)

  CONCN         0.0     0.012580   0.017820   0.025130   0.031630   0.037690   0.044500   0.045000   0.049400
  DEGREE         10        10         10          9          9         10         10         10         10
    0        425.60     424.06     423.49     421.77     419.29     416.74     414.06     413.09     409.45
    1          0.05      -0.60       0.41       1.23      -0.27      -2.21      -2.28      -2.70      -3.14
    2       -147.13    -125.15    -125.69     -96.35     -54.55     -30.65     -31.27     -33.20     -58.16
    3        -89.97     -45.59     -60.84     -67.14     -27.73       2.66     -21.94      -6.20     -12.22
    4        227.29      25.78      34.38    -152.21    -420.50    -509.08    -273.37    -147.68     321.20
    5        599.39     157.77     282.96     311.75      92.49    -131.05     149.83      63.78     160.27
    6       -945.05      27.15    -321.48     550.00    1248.31    1540.57     170.71    -554.03   -2530.91
    7      -1855.66    -351.45    -735.75    -827.43    -481.18     289.97    -655.43    -494.06    -777.74
    8       2335.69     -15.91     765.40    -616.62   -1265.83   -2148.54     820.70    2374.02    5629.99
    9       1974.37     307.47     693.99     818.13     750.76    -184.48     802.20     713.09     916.15
   10      -2346.91    -105.41    -771.97       0.0        0.0     1102.92   -1194.29   -2334.60   -4167.45
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INTERFACIAL TENSION (Y)

 SOLUTION           BASE        1          2          3          4          5          6          7          8
 CONCENTRATION               0.012580   0.017820   0.025130   0.031630   0.037690   0.044500   0.046000   0.049400
 ACTIVITY (C/CO)             0.254655   0.360729   0.508704   0.640283   0.762955   0.900810   0.931174   1.000000
 LN(C/CO)                     -1.3673    -1.0196    -0.6759    -0.4458    -0.2706    -0.1045    -0.0713     0.0
            VOLTS
           -0.600   387.67     387.39     387.20     387.10     387.00     386.87     386.62     386.56     386.02
           -0.550   393.27     392.82     392.58     392.39     392.24     392.14     391.80     391.71     391.09
           -0.500   398.21     397.85     397.58     397.26     396.93     396.98     396.62     396.50     395.73
           -0.450   402.96     402.53     402.25     401.83     401.41     401.44     401.01     400.82     399.65
           -0.400   407.41     406.82     406.51     406.06     405.61     405.45     404.81     404.49     402.68
           -0.350   411.44     410.69     410.32     409.83     409.35     408.90     407.90     407.40     404.85
           -0.300   414.97     414.12     413.66     413.08     412.50     411.70     410.24     409.57     406.35
           -0.250   418.00     417.07     416.51     415.76     414.96     413.80     411.89     411.08     407.39
           -0.200   420.56     419.53     416.90     417.91     416.76     415.25     412.98     412.08     408.17
           -0.150   422.64     421.49     420.83     419.55     417.99     416.14     413.63     412.69     408.77
           -0.100   424.23     422.91     422.26     420.73     418.76     416.60     413.97     413.02     409.22
           -0.050   425.24     423.78     423.17     421.47     419.17     416.77     414.10     413.15     409.46
            0.0     425.60     424.06     423.49     421.77     419.29     416.74     414.06     413.09     409.45
            0.050   425.22     423.71     423.19     421.58     419.13     416.55     413.86     412.87     409.14
            0.100   424.07     422.70     422.23     420.85     418.65     416.17     413.47     412.47     408.57
            0.150   422.14     421.02     420.58     419.51     417.74     415.48     412.82     411.84     407.77
            0.200   419.48     418.65     418.26     417.50     416.26     414.33     411.79     410.92     406.80
            0.250   416.18     415.61     415.29     414.79     414.09     412.56     410.29     409.60     405.67
            0.300   412.33     411.92     411.70     411.37     411.11     410.00     408.16     407.73     404.28
            0.350   407.98     407.62     407.53     407.27     407.26     406.55     405.28     405.12     402.43
            0.400   403.17     402.74     402.80     402.55     402.55     402.19     401.53     401.60     399.82
            0.450   397.85     397.34     397.53     397.26     397.07     396.99     396.81     397.00     396.09
            0.500   391.96     391.43     391.69     391.45     390.93     391.05     391.11     391.30     390.98
            0.550   385.41     385.00     385.26     385.12     384.29     384.53     384.51     384.62     384.46
            0.600   378.20     378.03     378.21     378.22     377.27     377.50     377.18     377.26     376.81
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SECOND ANALYSIS OF ELECTROCAPILLARY DATA FOR CYCLOHEXANOL
 IN 0.100N HCLO4 - DATA OF D. BROADHEAD (CONC=C/C0)


 INPUT PARAMETERS

   ORG                      ELECTR                  NAME
   CYCLOHEXANOL             IN 0.100N HCLO4         DATA OF D. BROADHEAD

   NCONCS     NVOLTS     VSTART       VINC       VECM        CC
        6         25     -0.600      0.050     -0.479     1.0000


 INPUT COEFFICIENTS FOR POLYNOMIALS

  CONCN         0.0     0.025000  0.050000  0.100000  0.225000  0.450000  0.900000
  DEGREE        10         9         9         10        10        10        10
    0        395.77    395.36    395.12    393.53    389.22    382.84    374.35
    1       -120.51   -118.72   -113.32    -94.31    -59.18    -36.26    -40.30
    2       -119.58   -120.08   -203.96   -277.91   -278.35   -198.31   -206.33
    3        -16.49     98.51    225.54     90.23   -347.77   -433.23   -281.42
    4        -26.36   -371.71    706.23   1412.50    854.26   -174.24    556.40
    5        105.00   -954.19   -795.72    679.18   2816.58   1461.01   1978.80
    6        120.24   1266.54  -4085.73  -5700.84    263.08   3284.89   -259.77
    7       -121.95   4526.81  -5135.50 -12232.21  -8173.93   2738.28  -7538.20
    8       -129.32   3859.16  -2824.87 -10645.27 -12650.88    508.44 -11566.28
    9         44.81   1082.64   -585.31  -4282.00  -7845.83   -516.83  -7309.87
   10         45.91   -105.41   -771.98   -636.71  -1812.40   -223.90  -1731.15


 COEFFICIENTS OF TRANSFORMED POLYNOMIALS
  (NOW IN TERMS OF VOLTS VS. ELECTROCAPILLARY MAXIMUM OF
  BASE ELECTROLYTE)

  CONCN         0.0     0.025000  0.050000  0.100000  0.225000  0.450000  0.900000
  DEGREE        10         9         9         10        10        10        10
    0        425.60    416.71    408.37    399.95    390.54    382.09    373.66
    1         -0.09     15.87     17.51     14.52     16.94     17.76     17.86
    2       -135.39    -42.00    -21.63    -21.50    -32.31    -25.74    -29.13
    3        -17.85   -172.91    -39.76     64.69      1.32     -9.16     -7.46
    4        102.60   -358.89   -245.50    -20.29    167.70     46.76    131.50
    5        -26.77    647.01   -294.13   -714.77     11.57     79.36    103.12
    6       -207.76    886.04    389.09   -583.40  -1208.51   -334.13   -944.73
    7        138.22  -1319.04    654.83   1588.66   -599.03   -526.14   -764.04
    8        151.54   -808.09   -301.60   1240.57   2459.80    424.74   2072.72
    9       -175.11   1082.64   -585.31  -1232.19    835.54    555.67    982.34
   10         45.91   -105.41   -771.97   -636.70  -1812.39   -223.90  -1731.15
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INTERFACIAL TENSION (Y)

SOLUTION	[illegible]	1	2	3	4	5	6
CONCENTRATION		0.025000	0.050000	0.100000	0.225000	0.450000	0.900000
ACTIVITY (C/CO)		0.025000	0.050000	0.100000	0.225000	0.450000	0.900000
LN(C/CO)		-3.6889	-2.9957	-2.3026	-1.4917	-0.7985	-0.1054
VOLTS							
-0.600	387.17	386.37	384.78	380.19	371.61	363.36	354.65
-0.550	392.74	391.49	389.08	382.93	373.82	365.54	357.04
-0.500	397.93	395.11	392.39	385.40	375.95	367.61	359.07
-0.450	402.71	400.27	395.07	387.54	378.01	369.59	361.05
-0.400	407.05	403.37	397.33	389.44	379.92	371.44	362.94
-0.350	411.07	406.65	399.30	391.17	381.65	373.17	364.69
-0.300	414.65	409.22	401.06	392.81	383.23	374.77	366.28
-0.250	417.81	411.06	402.63	394.36	384.68	376.25	367.74
-0.200	420.50	412.53	404.04	395.81	386.05	377.62	369.11
-0.150	422.68	413.75	405.29	397.10	387.34	378.90	370.40
-0.100	424.28	414.83	406.42	398.22	388.54	380.07	371.60
-0.050	425.27	415.83	407.44	399.16	389.61	381.14	372.69
0.0	425.80	416.71	408.37	399.95	390.54	382.09	373.66
0.050	425.26	417.37	409.19	400.63	391.31	382.92	374.48
0.100	424.23	417.67	409.84	401.24	391.93	383.61	375.16
0.150	422.53	417.43	410.24	401.79	392.43	384.17	375.72
0.200	420.17	416.49	410.24	402.23	392.84	384.62	376.18
0.250	417.17	414.71	409.67	402.43	393.15	384.94	376.55
0.300	413.56	412.01	408.34	402.19	393.29	385.11	376.80
0.350	409.35	408.40	406.07	401.22	393.11	385.06	376.80
0.400	404.55	403.93	402.72	399.25	392.35	384.67	376.40
0.450	399.16	398.70	398.23	396.03	390.71	383.74	375.35
0.500	393.18	392.82	392.65	391.43	387.85	381.99	373.41
0.550	386.60	386.35	386.14	385.50	383.51	379.11	370.36
0.600	379.40	379.31	378.93	378.50	377.62	374.80	366.12

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SECOND ANALYSIS OF ELECTROCAPILLARY DATA FOR CYCLOHEXANONE
 IN 0.100N HCLO4 - DATA OF D. BROADHEAD (CONC=C/CO)


 INPUT PARAMETERS

   ORG                         ELECTR                 NAME
   CYCLOHEXANONE               IN 0.100N HCLO4        DATA OF D. BROADHEAD

   NCONCS     NVOLTS     VSTART       VINC       VECM         CO
        4         25     -0.600      0.050     -0.482     1.0000


 INPUT COEFFICIENTS FOR POLYNOMIALS

  CONCN        0.0      0.050000  0.237500  0.475000  0.950000
  DEGREE       10          9         10        10        10
    0        395.95     393.93    386.01    379.64    371.73
    1       -120.74    -103.94    -60.67    -49.94    -49.12
    2       -120.73    -200.86   -226.25   -196.21   -201.88
    3         -6.83     137.11   -188.57   -191.80   -204.93
    4        -30.40     411.94    490.29    253.74    335.53
    5        -22.87    -580.06   1230.71    826.85   1086.96
    6        -75.30   -2008.19   -603.44   -175.38   -254.74
    7       -146.98   -1729.57  -4889.87  -2732.52  -4012.52
    8        -19.54    -497.66  -6515.90  -3712.72  -5786.48
    9         96.96      -2.08  -3733.21  -2101.46  -3498.56
   10         45.60       0.0    -812.84   -446.80   -798.82


 COEFFICIENTS OF TRANSFORMED POLYNOMIALS
  (NOW IN TERMS OF VOLTS VS. ELECTROCAPILLARY MAXIMUM OF
  BASE ELECTROLYTE)

  CONCN        0.0      0.050000  0.237500  0.475000  0.950000
  DEGREE       10          9         10        10        10
    0        425.60     403.16    385.94    378.13    369.86
    1          0.03      29.85     32.09     33.23     32.55
    2       -130.26     -30.57    -47.41    -45.11    -44.27
    3        -12.86     -51.69    -10.51     -9.73    -11.65
    4         66.82    -283.11     64.78     43.91     56.63
    5        -39.26    -103.96    -80.25    -77.61    -22.21
    6       -101.63     609.60   -588.76   -404.75   -503.63
    7        126.53     172.03    -65.30     11.84   -226.45
    8         36.57    -488.65   1180.91    732.26   1038.98
    9       -122.82      -2.08    184.66     52.13    351.74
   10         45.60       0.0    -812.84   -446.80   -798.82
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INTERFACIAL TENSION (Y)

 SOLUTION             BASE         1          2          3          4          5          6
 CONCENTRATION                0.025000   0.050000   0.100000   0.237500   0.475000   0.950000
 ACTIVITY (C/CO)              0.025000   0.050000   0.100000   0.237500   0.475000   0.950000
 LN(C/CO)                      -3.6889    -2.9957    -2.3026    -1.4376    -0.7444    -0.0513
            VOLTS
           -0.600    387.03                372.25                353.94     345.64     337.89
           -0.550    392.66                375.60                357.34     349.13     341.37
           -0.500    397.88                378.89                360.68     352.53     344.70
           -0.450    402.70                382.16                363.92     355.80     347.91
           -0.400    407.12                385.35                367.01     358.91     350.99
           -0.350    411.15                388.39                369.94     361.86     353.91
           -0.300    414.76                391.19                372.71     364.66     356.67
           -0.250    417.92                393.73                375.33     367.32     359.28
           -0.200    420.60                396.00                377.81     369.83     361.74
           -0.150    422.74                398.04                380.13     372.19     364.04
           -0.100    424.31                399.90                382.28     374.37     366.18
           -0.050    425.28                401.60                384.22     376.36     368.12
            0.0      425.60                403.16                385.94     378.13     369.86
            0.050    425.27                404.57                387.43     379.68     371.37
            0.100    424.29                405.76                388.67     381.00     372.66
            0.150    422.66                406.64                389.68     382.08     373.73
            0.200    420.38                407.05                390.43     382.92     374.56
            0.250    417.47     410.43     406.85                390.89     383.48     375.13
            0.300    413.94     409.75     405.88                390.99     383.70     375.38
            0.350    409.79     406.54     403.98     399.26     390.60     383.49     375.23
            0.400    405.04     402.46     401.05     397.00     389.58     382.73     374.53
            0.450    399.69     397.21     397.05     394.03     387.72     381.24     373.11
            0.500    393.74     391.37     392.00     389.82     384.84     378.87     370.78
            0.550    387.18     384.77     385.99     384.45     380.79     375.48     367.40
            0.600    380.00     377.93     379.16     378.12     375.51     370.96     362.88
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FRUMKIN EQUATION FIT TO ELECTROCAPILLARY DATA FOR
 3-PENTANOL           IN 0.100N HCLO4       DATA OF D. BROADHEAD
 ABSCISSA OF COMPOSITE PI VS. LN A CURVE IS LN A (-.033V VS.ECM)

 MAXIMUM SURFACE EXCESS = 4.470X10**(-10) MOLES/CM**2
 ACTIVITY FOR HALF COVERAGE = 1.650E-02
 ALPHA =  1.3364
 B-ZERO = 1.555E 01
 B-ZERO-PRIME = 0.2628
 EQUATION FOR ISOTHERM  LN(TH/(A*(1-TH))) = ( 2.6728)*TH + ( 2.744)
 EQUATION OF STATE  PI = (-14.808)*TH**2 + (-11.08)*LN(1-TH)

 SURFACE     THETA      LN A      LN A        A       A/AHALF      PI        PI
  EXCESS               (EXPTL)   (CALCD)   (CALCD)    (CALCD)    (EXPTL)   (CALCD)
   0.51      0.115     -5.00     -5.10     0.0061      0.36        0.7       1.2
   0.66      0.148     -4.90     -4.89     0.0075      0.45        0.8       1.5
   0.91      0.203     -4.80     -4.65     0.0095      0.56        1.0       1.9
   1.12      0.250     -4.70     -4.51     0.0110      0.65        1.3       2.3
   1.32      0.295     -4.60     -4.40     0.0122      0.72        1.6       2.6
   1.50      0.336     -4.50     -4.32     0.0133      0.78        2.0       2.9
   1.77      0.396     -4.40     -4.22     0.0146      0.87        2.4       3.3
   1.93      0.433     -4.30     -4.17     0.0154      0.91        2.8       3.5
   2.10      0.469     -4.20     -4.12     0.0162      0.96        3.3       3.8
   2.26      0.505     -4.10     -4.07     0.0170      1.01        3.8       4.0
   2.51      0.563     -4.00     -4.00     0.0184      1.09        4.5       4.5
   2.72      0.607     -3.90     -3.93     0.0196      1.16        5.1       4.9
   2.98      0.666     -3.80     -3.83     0.0216      1.28        5.8       5.6
   3.14      0.703     -3.70     -3.76     0.0233      1.38        6.6       6.1
   3.34      0.748     -3.60     -3.66     0.0259      1.53        7.3       7.0
   3.47      0.775     -3.50     -3.58     0.0279      1.65        8.2       7.6
   3.62      0.810     -3.40     -3.46     0.0315      1.86        9.1       8.7
   3.77      0.843     -3.30     -3.32     0.0363      2.15       10.0      10.0
   3.90      0.871     -3.20     -3.16     0.0424      2.51       11.0      11.5
   4.00      0.895     -3.10     -2.99     0.0502      2.97       12.0      13.1
   4.07      0.910     -3.00     -2.86     0.0570      3.37       13.0      14.4
   4.12      0.921     -2.80     -2.75     0.0637      3.77       15.0      15.5
   4.20      0.939     -2.60     -2.53     0.0800      4.73       17.0      17.9
   4.25      0.951     -2.40     -2.33     0.0977      5.78       19.1      20.0
   4.29      0.961     -2.20     -2.12     0.1203      7.12       21.3      22.2
   4.38      0.960     -2.00     -1.48     0.2277     13.47       23.5      29.0
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FRUMKIN EQUATION FIT TO ELECTROCAPILLARY DATA FOR
 CHLOROFORM             IN 0.10N HCLO4       DATA OF D. BROADHEAD
 ABSCISSA OF COMPOSITE PI VS. LN A CURVE IS LN ACT (0 V VS. ECM)

 MAXIMUM SURFACE EXCESS = 7.500X10**(-10) MOLES/CM**2
 ACTIVITY FOR HALF COVERAGE = 4.492E-01
 ALPHA =  1.8952
 B-ZERO = 3.345E-01
 B-ZERO-PRIME = 0.1503
 EQUATION FOR ISOTHERM  LN(TH/(A*(1-TH))) = ( 3.7904)*TH + (-1.095)
 EQUATION OF STATE  PI = (-35.235)*TH**2 + (-18.59)*LN(1-TH)

 SURFACE     THETA      LN A       LN A        A        A/AHALF     PI        PI
  EXCESS               (EXPTL)    (CALCD)   (CALCD)    (CALCD)   (EXPTL)   (CALCD)
   0.32      0.043     -2.40      -2.17     0.1142      0.25       0.5       0.8
   0.36      0.048     -2.20      -2.08     0.1252      0.28       0.6       0.8
   0.42      0.057     -2.00      -1.93     0.1448      0.32       0.8       1.0
   0.48      0.064     -1.80      -1.83     0.1602      0.36       1.1       1.1
   0.53      0.071     -1.60      -1.75     0.1746      0.39       1.3       1.2
   0.55      0.073     -1.52      -1.72     0.1787      0.40       1.4       1.2
   0.64      0.085     -1.44      -1.60     0.2016      0.45       1.6       1.4
   0.74      0.099     -1.36      -1.49     0.2262      0.50       1.7       1.6
   0.80      0.107     -1.32      -1.43     0.2388      0.53       1.8       1.7
   0.91      0.121     -1.28      -1.35     0.2601      0.58       1.8       1.9
   1.00      0.134     -1.24      -1.28     0.2780      0.62       2.0       2.0
   1.22      0.163     -1.20      -1.16     0.3137      0.70       2.1       2.4
   1.39      0.185     -1.16      -1.09     0.3366      0.75       2.2       2.6
   1.58      0.210     -1.12      -1.03     0.3587      0.80       2.3       2.8
   1.71      0.228     -1.08      -0.99     0.3715      0.83       2.5       3.0
   1.89      0.252     -1.04      -0.95     0.3876      0.86       2.7       3.2
   2.07      0.276     -1.00      -0.92     0.4005      0.89       2.9       3.3
   2.34      0.313     -0.96      -0.88     0.4156      0.93       3.1       3.5
   2.68      0.357     -0.92      -0.85     0.4290      0.95       3.4       3.7
   3.03      0.403     -0.88      -0.83     0.4381      0.98       3.6       3.9
   3.38      0.450     -0.84      -0.81     0.4443      0.99       4.0       4.0
   3.64      0.485     -0.80      -0.80     0.4478      1.00       4.3       4.0
   3.90      0.521     -0.76      -0.80     0.4512      1.00       4.7       4.1
   4.26      0.568     -0.72      -0.78     0.4565      1.02       5.1       4.2
   4.53      0.604     -0.68      -0.77     0.4620      1.03       5.5       4.4
   5.08      0.678     -0.64      -0.73     0.4818      1.07       6.0       4.9
   5.56      0.742     -0.60      -0.66     0.5162      1.15       6.5       5.8
   5.90      0.786     -0.56      -0.58     0.5582      1.24       7.1       6.9
   6.20      0.826     -0.52      -0.48     0.6159      1.38       7.7       8.5
   6.36      0.848     -0.48      -0.40     0.6701      1.49       8.4       9.7
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FRUMKIN EQUATION FIT TO ELECTROCAPILLARY DATA FOR
 CYCLOHEXANOL         IN 0.100N HCLO4      DATA OF D. BROADHEAD
 ABSCISSA OF COMPOSITE PI VS. LN A CURVE IS LN ACT (0 V VS. ECM)

 MAXIMUM SURFACE EXCESS = 5.000X10**(-10) MOLES/CM**2
 ACTIVITY FOR HALF COVERAGE = 1.306E-02
 ALPHA =  1.5943
 B-ZERO = 1.555E 01
 B-ZERO-PRIME = 0.2030
 EQUATION FOR ISOTHERM  LN(TH/(A*(1-TH))) = ( 3.1897)*TH + ( 2.744)
 EQUATION OF STATE  PI = (-19.761)*TH**2 + (-12.39)*LN(1-TH)

 SURFACE     THETA      LN A       LN A         A       A/AHALF      PI        PI
  EXCESS               (EXPTL)    (CALCD)    (CALCD)    (CALCD)    (EXPTL)   (CALCD)
   0.19      0.038      -6.00      -6.11      0.0022      0.17       0.2       0.4
   0.22      0.045      -5.80      -5.95      0.0026      0.20       0.4       0.5
   0.27      0.055      -5.60      -5.77      0.0031      0.24       0.6       0.6
   0.41      0.082      -5.40      -5.42      0.0044      0.34       0.7       0.9
   0.53      0.105      -5.30      -5.22      0.0054      0.41       0.8       1.2
   0.60      0.120      -5.20      -5.12      0.0060      0.46       1.0       1.3
   0.72      0.145      -5.10      -4.98      0.0069      0.53       1.1       1.5
   0.84      0.168      -5.00      -4.88      0.0076      0.58       1.3       1.7
   0.97      0.194      -4.90      -4.79      0.0083      0.64       1.5       1.9
   1.23      0.245      -4.80      -4.65      0.0096      0.73       1.8       2.3
   1.40      0.280      -4.70      -4.58      0.0102      0.78       2.1       2.5
   1.57      0.314      -4.60      -4.53      0.0108      0.83       2.5       2.7
   1.80      0.359      -4.50      -4.47      0.0115      0.88       2.9       3.0
   2.05      0.410      -4.40      -4.42      0.0121      0.93       3.4       3.2
   2.40      0.481      -4.30      -4.35      0.0129      0.98       4.0       3.6
   2.77      0.553      -4.20      -4.29      0.0136      1.04       4.6       3.9
   3.04      0.609      -4.10      -4.24      0.0144      1.10       5.4       4.3
   3.31      0.661      -4.00      -4.18      0.0152      1.17       6.1       4.8
   3.60      0.720      -3.90      -4.09      0.0167      1.28       7.0       5.5
   3.93      0.786      -3.80      -3.95      0.0193      1.48       8.0       6.9
   4.16      0.831      -3.70      -3.80      0.0224      1.71       9.0       8.4
   4.30      0.859      -3.60      -3.67      0.0254      1.94      10.0       9.7
   4.42      0.884      -3.50      -3.53      0.0293      2.24      11.1      11.3
   4.56      0.912      -3.40      -3.31      0.0364      2.79      12.2      13.7
   4.68      0.936      -3.20      -3.04      0.0479      3.67      14.6      16.8
   4.76      0.951      -3.00      -2.80      0.0606      4.64      17.0      19.6
   4.80      0.959      -2.80      -2.65      0.0710      5.44      19.3      21.5
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FRUMKIN EQUATION FIT TO ELECTROCAPILLARY DATA FOR
 CYCLOHEXANONE          IN 0.100N HCLO4       DATA OF D. BROADHEAD
 ABSCISSA OF COMPOSITE PI VS. LN A CURVE IS LN A (-0.7V VS. SCE)

 MAXIMUM SURFACE EXCESS = 4.660X10**(-10) MOLES/CM**2
 ACTIVITY FOR HALF COVERAGE = 5.918E-03
 ALPHA =  0.5737
 B-ZERO = 9.520E 01
 B-ZERO-PRIME = 0.5634
 EQUATION FOR ISOTHERM  LN(TH/(A*(1-TH))) = ( 1.1475)*TH + ( 4.556)
 EQUATION OF STATE  PI = ( -6.626)*TH**2 + (-11.55)*LN(1-TH)

 SURFACE     THETA      LN A       LN A         A        A/AHALF      PI          PI
  EXCESS               (EXPTL)    (CALCD)     (CALCD)    (CALCD)    (EXPTL)     (CALCD)
   0.59      0.126      -7.00      -6.63      0.0013      0.22        0.8         1.5
   0.62      0.133      -6.80      -6.59      0.0014      0.23        1.1         1.5
   0.69      0.148      -6.60      -6.48      0.0015      0.26        1.4         1.7
   0.77      0.165      -6.40      -6.37      0.0017      0.29        1.8         1.9
   0.80      0.172      -6.20      -6.32      0.0018      0.30        2.1         2.0
   0.84      0.181      -6.10      -6.27      0.0019      0.32        2.3         2.1
   0.95      0.204      -6.00      -6.15      0.0021      0.36        2.6         2.4
   1.04      0.224      -5.90      -6.06      0.0023      0.40        2.9         2.6
   1.12      0.241      -5.80      -5.98      0.0025      0.43        3.1         2.8
   1.18      0.254      -5.70      -5.93      0.0027      0.45        3.4         3.0
   1.37      0.293      -5.60      -5.77      0.0031      0.53        3.7         3.4
   1.59      0.340      -5.50      -5.61      0.0037      0.62        4.0         4.0
   1.88      0.403      -5.40      -5.41      0.0045      0.75        4.5         4.9
   2.25      0.482      -5.30      -5.18      0.0056      0.95        5.0         6.1
   2.46      0.528      -5.20      -5.05      0.0064      1.08        5.7         6.8
   2.65      0.568      -5.10      -4.94      0.0072      1.21        6.2         7.6
   2.93      0.628      -5.00      -4.75      0.0086      1.46        7.0         8.8
   3.06      0.656      -4.90      -4.66      0.0094      1.59        7.8         9.5
   3.11      0.668      -4.80      -4.62      0.0098      1.66        8.5         9.8
   3.19      0.684      -4.70      -4.57      0.0104      1.76        9.2        10.2
   3.22      0.692      -4.60      -4.54      0.0107      1.80       10.0        10.4
   3.30      0.708      -4.50      -4.48      0.0113      1.91       10.9        10.9
   3.41      0.731      -4.40      -4.40      0.0123      2.08       11.8        11.6
   3.51      0.754      -4.30      -4.30      0.0135      2.29       12.6        12.4
   3.60      0.774      -4.20      -4.22      0.0148      2.50       13.5        13.2
   3.69      0.793      -4.00      -4.12      0.0162      2.73       15.3        14.0
   3.86      0.828      -3.80      -3.93      0.0196      3.31       17.2        15.8
   3.99      0.856      -3.60      -3.76      0.0234      3.95       19.1        17.5
   4.09      0.878      -3.40      -3.59      0.0277      4.67       21.1        19.2
   4.21      0.903      -3.20      -3.36      0.0347      5.86       23.2        21.5
   4.26      0.914      -3.00      -3.24      0.0392      6.62       25.3        22.8
   4.34      0.931      -2.80      -3.02      0.0487      8.23       27.4        25.1
   4.40      0.944      -2.60      -2.82      0.0596     10.08       29.7        27.3
   4.48      0.961      -2.40      -2.46      0.0852     14.40       31.9        31.3
   4.55      0.975      -2.20      -1.99      0.1360     22.99       34.0        36.5
   4.59      0.985      -2.00      -1.50      0.2239     37.84       36.3        42.1
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APPENDIX D

Tables Cited in Text

Table 1. Precision of the electrocapillary curves

Adsorbate (activity)	Maximum Correction Applied for Evaporation (dynes/cm)	RMS Deviation (dynes/cm)	Percentage of Points with Error > 0.1 dyne/cm
3-Pentanol			
0	---	0.16	31
0.008	---	0.25	56
0.021	---	0.34	66
0.041	---	0.45	94
0.079	---	0.62	78
0.157	---	1.63	75
0.393	---	0.84	67
0.786	---	0.75	64
Chloroform			
0	---	0.18	30
0.225	0.13	0.14	20
0.361	0.13	0.10	28
0.509	0.40	0.14	42
0.640	0.36	0.24	43
0.763	0.56	0.17	35
0.901	1.03	0.22	40
0.931	0.88	0.25	48
1.000	0.72	0.27	59
Cyclohexanol			
0	---	0.02	0
0.025	---	0.12	34
0.050	0.76	0.22	48
0.100	0.71	0.14	55
0.225	0.25	0.09	17
0.450	0.07	0.04	3
0.900	---	0.06	7
Cyclohexanone			
0	---	0.03	0
0.025	---	0.06	5
0.050	---	0.15	60
0.100	---	0.02	0
0.238	---	0.05	7
0.475	---	0.05	7
0.950	---	0.03	0

Table 2. Orientation of molecules

Adsorbate	Configuration	Γ_m x 10^{10} (mole/cm^2)	Area/molecule ($Å^2$) (experimental)	Area/molecule ($Å^2$) (calculated)
Chloroform	---	7.50	22.1	19.3
3-Pentanol	Parallel	4.47	37.1	35
Cyclohexanol	axial OH	5.00	33.2	20
Cyclohexanol	equatorial OH	5.00	33.2	30
Cyclohexanone	parallel	4.66	35.6	26