

**COMPUTER PROGRAM FOR THERMODYNAMIC ANALYSIS OF ELECTROCAPILLARY DATA**

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**ABSTRACT**

Computer program for analysis of experimental interfacial tension to evaluate excess charge density, relative surface excess of the organic sorbate and differential capacitance are briefed. Orthogonal moving polynomial fitting, least square method of smoothing the experimental data and the statistical evaluation of method of fitting are reported. The developed program is tested for the reported results.

**Key words:** Interfacial tension, computer program, charge density.

**INTRODUCTION**

Electrosorption of organic substances on the properties of the electrode-solution interface is studied widely in important fields of electrochemistry as electrosynthesis, electrocatalysis, fuel cells, and corrosion inhibition. To understand the mechanism of electrosorption, experimental measurements with electrocapillary and differential capacitance set ups are made. Using the basic Gibbs adsorption equation, the thermodynamic relation between the variables at an electrified interface is evaluated. The charge density ( $q$ ) is found from the first derivative of the electrocapillary curve and the capacity ( $c$ ) of the double layer can be obtained from the second derivative of the electrocapillary curve. Surface excess of organic adsorbate is determined from the first derivative of surface tension with respect to logarithm of concentration of added organic substance. Fractional surface coverage, the fitting of isotherm, calculation of standard free energies of adsorption and polarizability of the molecule are carried out from the above analysed data.

**THERMODYNAMIC EQUATIONS**

The electrocapillary equation used in the analysis is given by equation (1)

$$d\gamma = -q^M dE - \Gamma_o d\mu_o \quad \dots\dots\dots (1)$$

where  $\gamma$  = interfacial tension  
 $q^M$  = excess charge density on the mercury surface  
 $E$  = Electrode potential  
 $\Gamma_o$  = Relative surface excess of the organic sorbate  
 $\mu_o$  = Chemical potential in the solution

To evaluate  $q^M$  and  $\Gamma_o$  using electrocapillary study, interfacial tension are measured at various concentrations of organic substance.  $q^M$ ,  $\Gamma_o$  and  $c$  are evaluated using the equations given below.

$$q^M = - \left( \frac{\delta \gamma}{\delta E} \right) \mu_o \quad \dots\dots\dots (2)$$

$$\Gamma_o = - \left( \frac{\delta \gamma}{\delta E} \right) E$$

$$= - \frac{1}{RT} \left( \frac{\delta \gamma}{\delta \ln d_o} \right) E \quad \dots\dots\dots (3)$$

where  $a_o$  = activity of the organic sorbate in solution

$$c = \left( \frac{\delta q^M}{\delta E^2} \right) \mu_o$$

$$= - \left( \frac{\delta^2 \gamma}{\delta E^2} \right) \mu_o \quad \dots\dots\dots (4)$$

where  $c$  = Differential capacitance (which experimentally can be measured)

**ANALYSIS**

In general, adsorption of organic compound can be determined either by interfacial tension or by differential capacitance measurements. The analysis of data obtained by measuring interfacial tension is more difficult than analysis of data obtained by measuring differential capacitance. Experimental results of capacitance are integrated to obtain  $q$ . Integration smooths the data. For evaluation of equations (2), (3) and (4) the mathematical process involved is differentiation which tends to magnify random errors.

For differentiation, the methods available are graphic method, numerical differentiation and method of least squares. Graphical procedure is tedious and inherently inaccurate and leads to serious question in the interpretation of experimental results. Normal numerical differentiation requires equal intervalled data. For quick and accurate analysis, many computational procedures based on method of least squares have been reported. Mainly two types of differentiation methods were considered.

(1) Those in which a curve was fitted to the data over the whole range of the independent variable  $E$ , and (2) those in which a curve was fitted to a segment which contained a fixed number of data points and which was moved over the range of  $E$ , one point being added and one deleted per move consecutively known widely as moving polynomial method.

The reported methods do not give the complete computer listing and do not reveal the inherent difficulties involved with each method of analysis. Many [1,2,4,5] accept the fact that their developed program may not work in another environment even though their routines have been used successfully in their laboratories with the additional checks. Here we report the programs developed in BASIC language so that any electrochemical scientist can use the analysis in any microcomputer system. The developed program has the flexibility in introducing weighing function, selection of various polynomials and smoothing routines. For relative comparison of each technique, results obtained using other reported programs are also presented.

**METHOD OF LEAST SQUARES**

Polynomial curve of degree M for N points of observation is fitted in the form of equation (5). (M < N)

$$V = K_0 + K_1 E + K_2 E^2 + \dots + K_M E^M \dots \quad (5)$$

By applying least squares criterion, normal equations are derived. It is written in the matrix form

$$[A][K] = [B] \dots \dots \dots (6)$$

where [A] and [B] are a function of r and E and the coefficient matrix [K] is evaluated by inverting [A]. When the determinant [B] tends to be very small, the solution of the coefficient matrix [K] is likely to be uncertain [3,6].

Recently many workers have started using orthogonal polynomials for determining least squares polynomial coefficients. The method involves in constructing a set of polynomials  $\phi_0(x), \phi_1(x), \dots, \phi_r(x)$  such that each member is orthogonal to all others in the set relative to a specified weighing function w(x). Thus we require a polynomial of  $\phi_j(x)$  of degree r such that  $\int w(x)\phi_r(x)\phi_k(x) dx = 0$  for  $r \neq k$ . Here a three term recurrence relation is used to generate the orthogonal polynomial (6). In general jth polynomial is defined over the x data point by

$$\phi_j(x) = x \cdot \phi_{j-1}(x) - \alpha_j \phi_{j-1}(x) - \beta_j \phi_{j-2}(x) \dots \dots \dots (7)$$

where  $\alpha_j$  and  $\beta_j$  are evaluated by the following equations

$$\alpha_{j+1} = \frac{\sum W(x) \phi_j^2(x) x \cdot (x)}{\sum W(x) x \cdot \phi_j^2(x)} \dots \dots \dots (8)$$

$$\beta_{j+1} = \frac{\sum W(x) \cdot x(I) \times \phi_j(x) \cdot \phi_{j-1}(x)}{\sum W(x) \times \phi_{j-1}^2(x)} \dots (9)$$

The columns  $\alpha_j$  and  $\beta_j$  can therefore generate the value of these polynomials recursively. The value of Y is computed by selecting the polynomials  $\phi_j(x)$

$$V = \sum_j C_j \phi_j(x) \dots \dots \dots (10)$$

where coefficient matrix is evaluated using the expression using orthogonal property

$$COEF(K) = \frac{\sum \phi_k(I) \times Y(I) \times W(I)}{\sum (\phi_k(I))^2 \times W(I)} \dots \dots (11)$$

After evaluating the coefficients and polynomials equation (10) is reduced to the form (5) and first and second differentials are evaluated as follows for Mth degree fitting substituting corresponding E values.

$$\left. \begin{aligned} \frac{\delta V}{\delta E} &= K_1 + 2K_2 E + 3K_3 E^2 + \dots + M \times K_M E^{M-1} \dots \\ \frac{\delta^2 V}{\delta E^2} &= 2K_2 + 6K_3 E + \dots + M(M-1)K_M E^{M-2} \dots \end{aligned} \right\} \dots (12)$$

**SMOOTHING**

The least squares approach is used to obtain a smoothed polynomial before differentiating. This process minimizes the sum of the squares of the residuals of the original data at the sample points but says nothing about the behaviour between the sample points. Thus, while we can hope that the derivative is estimated accurately, we are not in a very good position to be sure that the least squares polynomial does not have some wiggles between the sample points which will greatly influence the estimate of the derivative.

Differentiation method is quite sensitive to experimental errors in the values of interfacial tension. Smoothing has been obtained by applying least squares parabolic fitting to moving segments of the electrocapillary curve. Various smoothing formulae (3,4) are available. Here mostly first degree least squares approximation relevant to three points is used or the fitted values using high degree polynomial are used.

Various statistical tests like maximum, minimum error in fitting, variance estimation etc. are being applied to test the quality of fitting [2,4]. Here maximum and minimum error estimation alone is done as variance averages the variation.

**RESULTS AND DISCUSSION**

After developing the above programs, the results of reference 1 is tested for fitting. Figure 1 gives the computer print out of analysed case with reference to Table I. Close match in q and calculation could be seen. It is reported that Parsons et al calculated relative surface excesses from surface tension-activity data by fitting the data points over the whole range to a cubic equation. For the sake of comparison, Mohliner method of "Cubic fitting" is also applied for fitting. Table I summarises the percentage error obtained in the various cases analysed. It is found that various smoothing routines do not improve the fitting very well in the case of reference 1.

The various cases tried are: (1) simple moving cubic fit (2) cubic fit with one smoothing (3) cubic fit with two smoothing (4) moving orthogonal cubic fit (5) moving orthogonal cubic fit with one smoothing (6) moving orthogonal cubic fit with two smoothing and moving orthogonal of various degrees and various weighing functions. With orthogonal polynomial fitting, the first differential - Q fitting error could be brought down to zero as shown in Table I. While with Mohliner cubic fit (2), the error was in the range of 3.4%. The second differential - C fitting error was in the range of 14% while with moving cubic fit (2), the maximum error was in the range of 20%. It is found that the developed program is a flexible one with the capability of doing either (1) moving orthogonal third or any degree fitting or (2) single polynomial fitting of any degree with weighing function. From the overlaying facility, the gross fitting of the results could be decided in a better way.

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(r) (Q) (C)  
440 30 240

FIG - 1

TABLE-1: ELECTROCAPILLARY CURVES (CASE No:1)

X AXIS: -E (Volts)

Y AXIS: GAMA (dyn/cm); Q (micro Cou/cm<sup>2</sup>); C (micro Far/cm<sup>2</sup>)

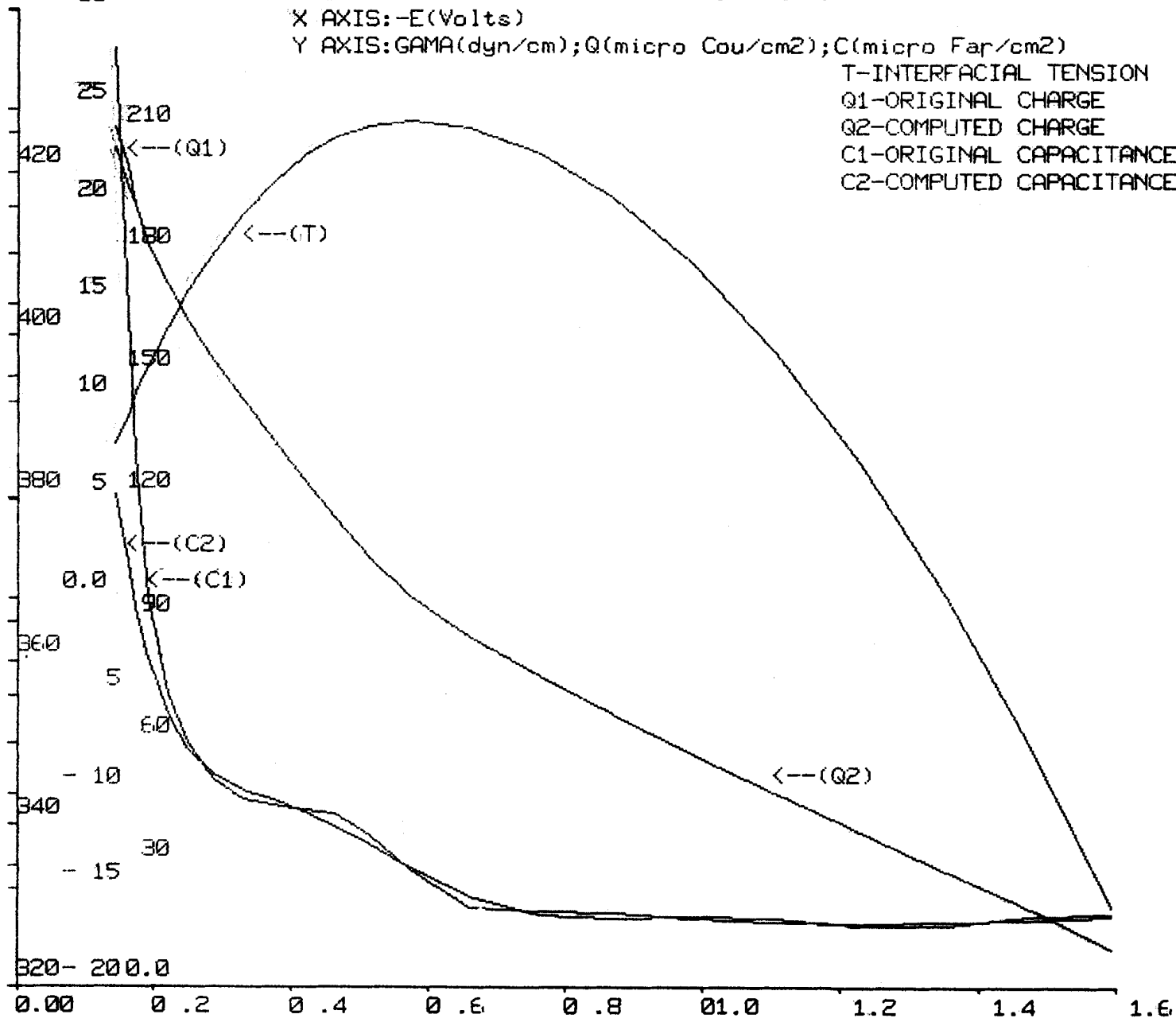
T-INTERFACIAL TENSION

Q1-ORIGINAL CHARGE

Q2-COMPUTED CHARGE

C1-ORIGINAL CAPACITANCE

C2-COMPUTED CAPACITANCE



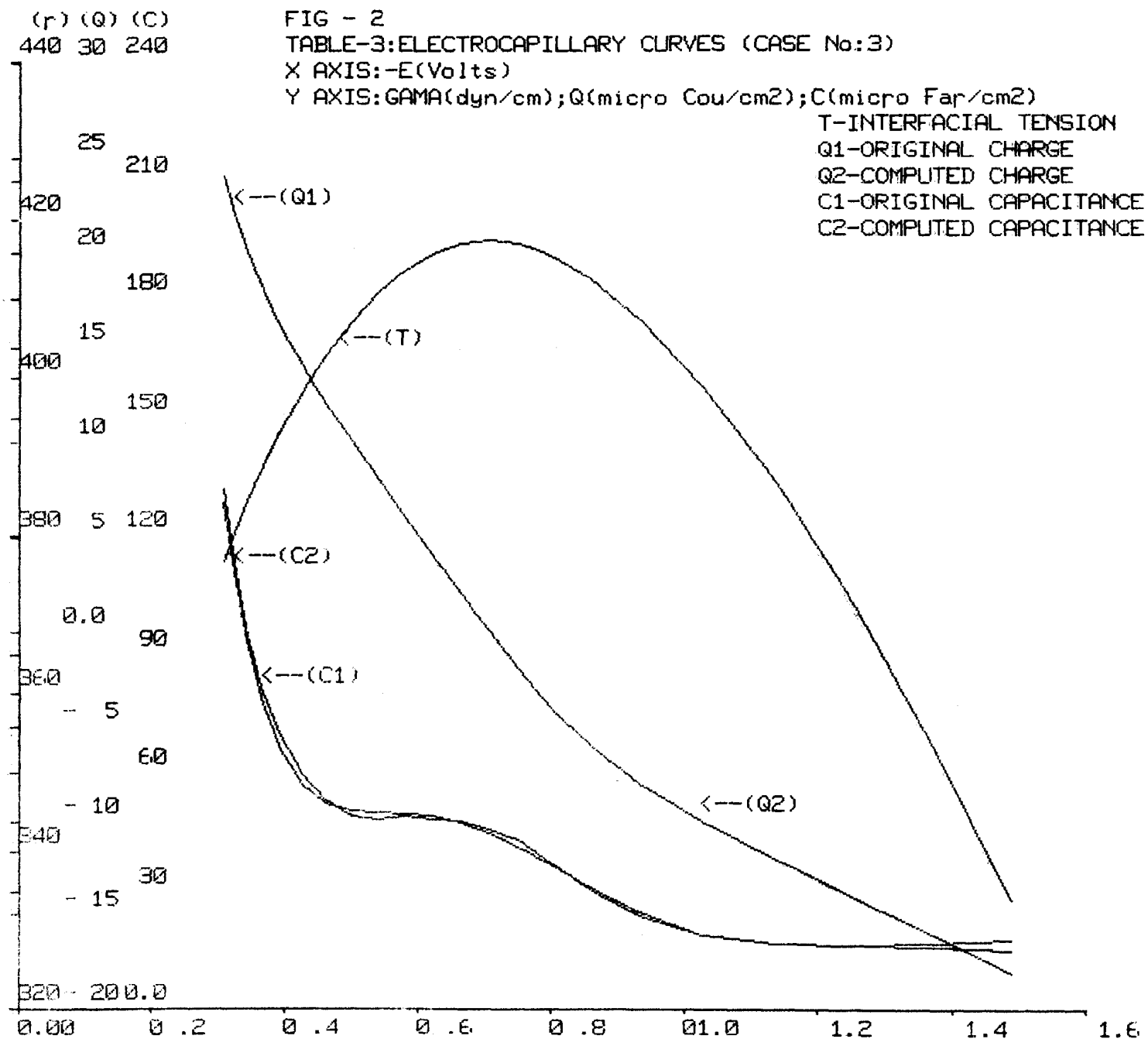


Table I: Estimation of error between reported [1] and computed results with orthogonal curve fitting

		Gamma ( $\gamma$ )	Max % Error		Degree Method of fitting
			Charge (Q)	Capacitance(C)	
1. 0.01M KBr in water	Potential E vs original values of $\gamma$ , Q, C and computed values of $\gamma$ , Q, C (Table1; Ref:1)	0.133	0	14	10 Fitting $\gamma$ to get Q & C
2. 0.1M KBr in water	-do- (Table 2; Ref:1)	0.835	0	13.03	10 -do-
3. 1.0M KBr in water	-do- (Table 3; Ref:7)	0.064	0	3.6	10 -do-
4. 0.01M KBr in water	Potential E vs original capacitance and computed capacitance (Table 7; Ref:1)	—	—	9.61	10 Fitting charge to get C
5. 0.1M KBr in water	-do- (Table 2; Ref:1)	—	—	5.8	8 -do-
6. 1.0M KBr in water	-do- (Table 3; Ref:1)	—	—	3.4	8 -do-
7. 0.01M KBr in water	Potential vs original capacitance and two time fitted C (Table 1; Ref:1)	—	—	10.62	10 Fitting computed Q to get C
8. 0.1M KBr in water	-do- (Table 2; Ref:1)	—	—	9.4	8 -do-
9. 1.0M KBr in water	-do- (Table 3; Ref:1)	—	—	3.4	8 -do-

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