

CALCULATION OF ADSORPTION-RELATED PARAMETERS FROM A.C. POLAROGRAPHIC DATA: Basis and Computer Programs

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SUMMARY

Phase-selective alternating current polarography can be advantageously used for the observation and quantitative description of adsorption at a solution—electrode interface; for example, in the absence of a faradaic process, the quadrature current component is simply related to the interfacial differential capacity. Such a.c. measurements are especially advantageous for the occasional investigation of adsorption. The basis of using such measurements is considered; the data analysis is examined; specifics for computer calculation of differential capacity, surface charge density, and relative surface excess, and the requirements for data smoothing are described. The computer programs developed are sufficiently general for handling special situations.

The thermodynamic properties of and conceptual models for the electrical double layer have been reviewed [1–6], as have experimental and theoretical progress in double-layer research and remaining problems [7, 8], the experimental measurement of adsorption at electrodes [9], and the adsorption of organic compounds [10–12]. However, most electrochemists seem to avoid detailed adsorption studies, probably because of (a) the tedium of employing either a capillary electrometer to obtain interfacial surface tension data or an a.c. impedance bridge to obtain differential capacitance data, (b) the difficulty involved in precise and accurate determinations of the potential of zero charge (p.z.c.) [13] and of surface tension at the p.z.c., and (c) the quite lengthy analysis of experimental double-layer data.

Although digital computers have made the data analysis less arduous, computer program development can be very costly in terms of man-hours and computer expense, particularly for one with limited experience in programming. Mohilner and Mohilner [14] have discussed the basis for curve fitting and data smoothing with emphasis on electrocapillary data analysis;

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no main program for combining the subroutines to form a complete program is given and the smoothing routines may be more sophisticated than necessary for capacitance-data analysis. MacDonald [15] has described a program for the determination, based on capacitance data, of relative surface excesses of uncharged species, which totally desorb at one potential extreme before the onset of faradaic activity; the program is not mathematically flexible in terms of handling special situations.

In an attempt to minimize the difficulties indicated, various methods of data analysis, based on alternating current (a.c.) polarography as a means of data acquisition, have been compared with the aim of developing the most efficient combination of data acquisition and analysis which would meet the needs of routine adsorption studies.

In the absence of faradaic current, the quadrature current component obtainable on phase-selective a.c. polarography (as well as the total a.c.) is capacitive and directly related to the differential capacity. As a.c. polarography is basically an automated non-nulling version of a.c. bridge measurement, it should have the advantages of the bridge method except for the slight loss in precision inherent in techniques which do not employ null detection. Phase-selective a.c. polarographs are commercially available and are becoming quite common.

Computer programs were developed for analyzing data on uncharged adsorbates; these are sufficiently general for handling most special situations. Because of space limitation, the programs are not given; program listings or decks can be made available. Because some investigators may desire to develop comparable programs to meet special requirements or may find the programming language employed (FORTRAN IV) unacceptable, precautions are noted which must be observed in efficient and successful programming of adsorption data analysis.

MATHEMATICAL BASIS

The physical situation involves an electrochemical cell, in which the solution to be investigated contains solvent, supporting electrolyte (including buffer if necessary), and the uncharged adsorbate of interest with only the adsorbate concentration being varied. The applied potential is varied over the range of interest and capacitance data are acquired in the form of capacity-current magnitudes, e.g., a.c. polarographic quadrature-current components.

The capacity current, I_c , is converted to capacitance, C' , and then to differential capacitance, C :

$$C' = I_c / (2 \pi f U_{ac}); C = C' / A$$

where f is the frequency in Hz of the applied alternating voltage, U_{ac} is its amplitude in V (peak or r.m.s. depending on the instrumental current display utilized), and A is the electrode area.

The relations between C and electrode charge, q , and between q and

interfacial surface tension, γ , are given [3] by

$$q = q' + \int_{E'}^E C \, dE \text{ and } \gamma = \gamma' - \int_{E'}^E q \, dE \quad (1)$$

where q' is the charge at any arbitrary starting potential E' , and where γ' is the surface tension at E' . The relation between relative surface excess, Γ , and γ is given [3] by

$$\Gamma = -(\partial\gamma/\partial\mu)_E \quad (2)$$

A computer must work with these five equations to calculate relative surface excesses from a.c. capacity current data.

The commonest choice of E' is the p.z.c.: $E' = E_z$. Then, $\gamma' = \gamma_z$ and, by definition, $q' = 0$. Equations (1) are then written as

$$q = \int_{E_z}^E C \, dE \text{ and } \gamma = \gamma_z - \int_{E_z}^E q \, dE \quad (3)$$

To apply eqns. (2) and (3) it is necessary to obtain capacitance data for each adsorbate concentration involved, and to determine E_z and γ_z at each concentration. In a second possibility [15, 16], if a potential region exists in which complete desorption has occurred for all investigated concentrations and faradaic activity is absent, then $\Gamma = 0$ within this potential region and, from eqn. (2) $(\partial\gamma/\partial\mu)_E = 0$. Additionally, within the potential region of complete desorption, $(\partial q/\partial\mu)_E = 0$. If integration of eqns. (1) is begun within that region, then $E' = E_l$, $q' = q_l$, and $\gamma' = \gamma_l$ (subscript l refers to a specific potential at which desorption is complete at all concentrations); by defining a parameter $q^* = q - q_l$, eqns. (1) may be rewritten as

$$q^* = \int_{E_l}^E C \, dE \quad (4)$$

$$\gamma = \gamma_l - \int_E^E q^* \, dE - \int_{E_l}^E q_l \, dE \quad (5)$$

Based on eqns. (2) and (5), Γ is given by

$$\Gamma = -(\partial\gamma_l/\partial\mu)_E + \left[(\partial/\partial\mu) \int_{E_l}^E q^* \, dE \right]_E + \left[(\partial/\partial\mu) \int_{E_l}^E q_l \, dE \right]_E \quad (6)$$

Since γ_l and q_l are independent of adsorbate concentration (see above), eqn. (6) reduces to

$$\Gamma = \left[(\partial/\partial\mu) \int_{E_l}^E q^* \, dE \right]_E \quad (7)$$

If a "relative" surface tension is defined as $\gamma^* = \int_{E_l}^E q^* \, dE$, then eqn. (7) may be rewritten as

$$\Gamma = (\partial\gamma^*/\partial\mu)_E \quad (8)$$

It can be shown that, within the potential region for which $(\partial\gamma/\partial\mu)_E = 0$, $(\partial C/\partial\mu)_E = 0$; hence, coincidence of the capacitance curves, independent of adsorbate concentration, is an experimentally observable verification for the applicability of eqns. (4) and (8). Coincidence of the capacitance curves at one potential should not be adjudged as confirming the applicability; coincidence of all capacitance curves over a finite potential range is necessary.

PROGRAMS DEVELOPED

The general formula involved in a least-squares fit, $y = \sum_{i=0}^n \pi_i x^i$, is a power-series relation between independent variable, x , and dependent variable, y , with the coefficients, π_i , to be determined. The relations involved (capacitance and charge as a function of potential) in the case of a quadratic polynomial are as follows (the π coefficients differ for the parameter involved):

$$C = \pi_0 + \pi_1 E + \pi_2 E^2 \quad (9)$$

$$q = \pi_0 + \pi_1 E + \pi_2 E^2 \quad (10)$$

Because the chemical potential is generally unknown, it is necessary to express eqns. (2) and (8) in terms of activity, a , or concentration, c , through the equation $\mu = \mu^0 + RT \ln a$. At constant ionic strength, the activity coefficient of the adsorbate is independent of adsorbate concentration; hence, $d(\ln a) = d(\ln c)$, and $d\mu = RT d(\ln c)$. Substituting this equation into eqn. (2) yields

$$\Gamma = -(1/RT) [\partial\gamma/\partial(\ln c)]_E \quad (11)$$

Thus, the polynomial necessary for least-squares analysis is

$$\gamma = \pi_0 + \pi_1 \ln c + \pi_2 (\ln c)^2 \quad (12)$$

Equations (9), (10) and (12) are also the basis for all least-squares curve smoothing, interpolating, integrating and differentiating involving C' , q^* and γ^* , respectively.

Procedures for performing a least-squares fit can be found in numerical analysis books [17]. Figures 1 and 2 give general flow diagrams for setting up the least-squares-matrix equation and for its solution by the Gauss—Jordan method of upper triangulation.

Smoothing and interpolating program

Some smoothing of a.c. polarographic capacity-current data is advisable because these data lack the precision of a.c. impedance-bridge data and small errors may occur in reading the x—y recorder plots. Additionally, within potential regions of smooth capacitance variation, data can be supplied to the program at large potential increments and more closely-spaced interpolated values can be calculated from the smoothing functions, saving considerable man-hours of reading recorder plots and key-punching data.

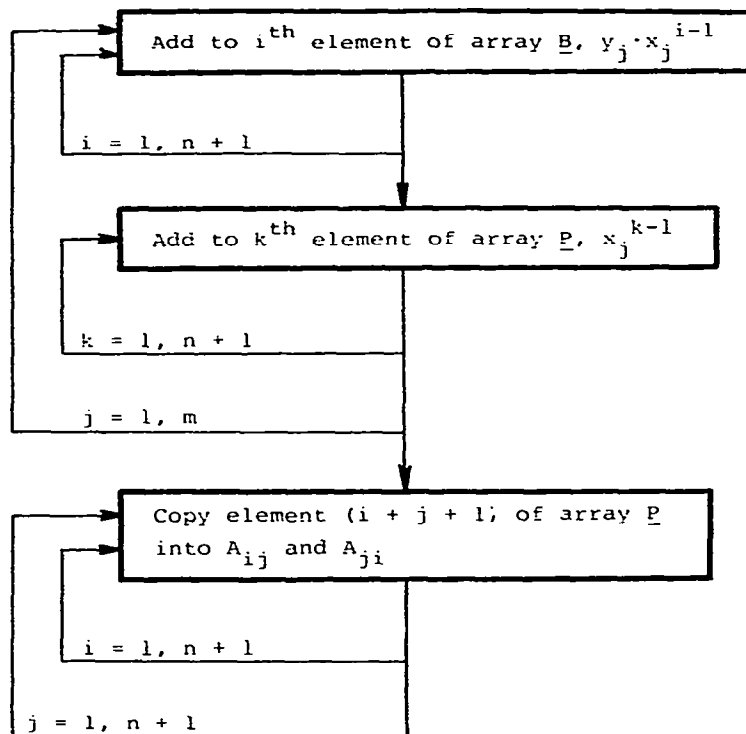


Fig. 1. Procedure for assembling the least-squares matrix, $A\pi = B$.

Because a seriously faulty point can bias a curve fit, a computer-controlled check of each data point is recommended before curve fitting. The procedure described (Fig. 3) separately checks all data points for each concentration except the first and last. Because the computer cannot distinguish fine structure in the data from faulty data points, only regions showing an apparent minimum or maximum ("minimax") in the data can be tested; therefore, as the program proceeds sequentially through the data, any point, C'_i , for which the criterion $C'_{i-1} \leq C'_i \leq C'_{i+1}$ or $C'_{i-1} \geq C'_i \geq C'_{i+1}$ is satisfied, is assumed correct, and the program proceeds to check data point C'_{i+1} . If the criterion mentioned is not satisfied, an apparent "minimax" at E_i is indicated. Since a true minimax shows a decreasing slope as the minimum or maximum point is approached, then the criteria

$$\Delta_i/\Delta_{i-1} > 0; |\Delta_{i-1}| > |\Delta_i|; \Delta_{i+2}/\Delta_{i+1} > 0; |\Delta_{i+2}| > |\Delta_{i+1}| \quad (13)$$

(where Δ is the slope of a straight line connecting the point indicated and the preceding point) can be used to determine whether a true minimax occurs at E_i . If these conditions are satisfied, C'_i is assumed to be correct. A faulty point at E_i is easily corrected by calculation of a capacitance value at E_i from a curve fit to the adjacent points, (E_{i-1}, C'_{i-1}) and (E_{i+1}, C'_{i+1}) . If the quadratic fit is used, the third point required can be determined from

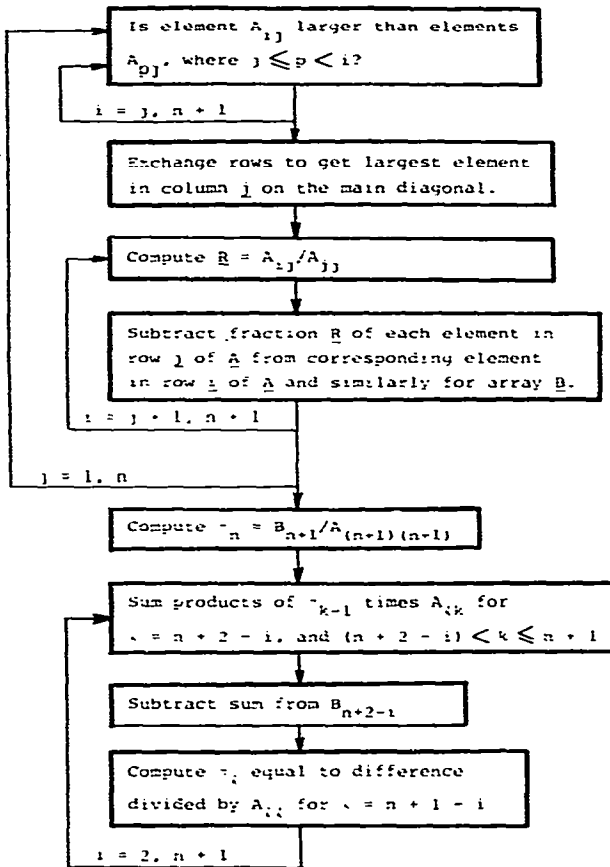


Fig. 2. Solution of n^{th} degree polynomial least-squares matrix equation, $A\pi = B$, for values of π_i .

$|\Delta_{i-1}| - |\bar{\Delta}| = K$; $|\Delta_{i-2}| - |\bar{\Delta}| = J$, where $\bar{\Delta}$ is the slope of a line connecting (E_{i-1}, C'_{i-1}) and (E_{i+1}, C'_{i+1}) . If $K < J$, the third point is (E_{i-2}, C'_{i-2}) ; otherwise, the third point is (E_{i+2}, C'_{i+2}) .

Next, the data are smoothed and interpolated by using a least-squares moving polynomial fit to eqn. (9), i.e., m data points are fitted k points at a time ($k < m$) with each fit corresponding to a progression of l points farther into the data ($l < k$); the options available are the values of k , l , and n (the degree of the fit). Figure 4 shows various possibilities for a moving quadratic polynomial fitting four points at a time. Low-order polynomials are preferable, particularly the quadratic case ($n = 2$), and one degree of smoothing is generally sufficient, so that $k = n + 2$ [14]. For optimum smoothing, l should be 1. With the exception of data points 1, 2, $m - 1$, and m , all points are fitted by more than one polynomial (two for $k = 4$) (cf. curve C, Fig. 4); averages of the values generated by each fit add to the smoothness of the data.

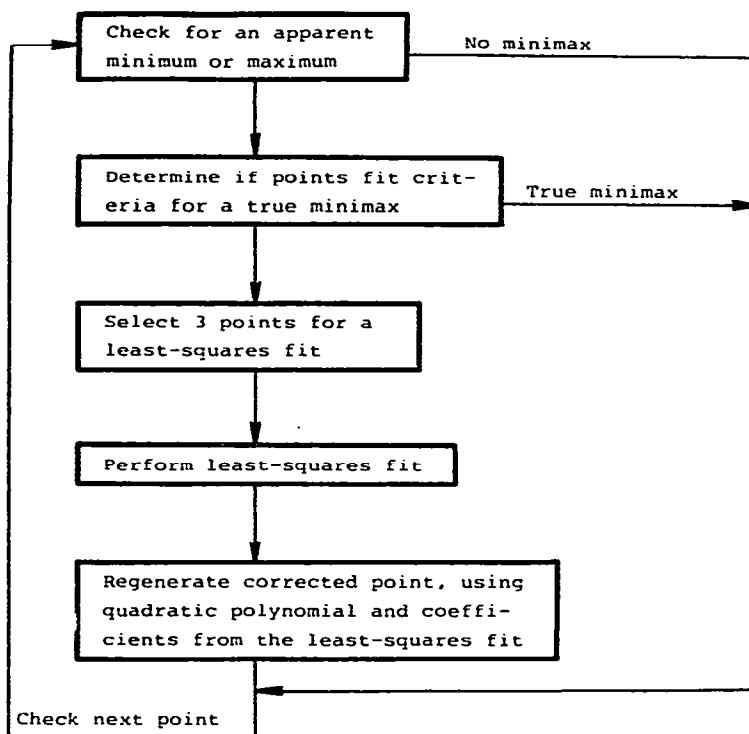


Fig. 3. Check of raw capacitance data to isolate and to correct faulty points.

For each fit, it is acceptable to generate smoothed capacitance data at any potential within the potential region defined by the fitted data points; however, because one or more degrees of smoothing are permitted, the polynomial need not perfectly follow the data points, and the data trend beyond the limits of the points being fitted has no effect on the curve fit. The combination of these two facts indicates that values generated near the potential range extremes may not tend smoothly toward the data outside this range. Therefore, the region in which values are to be generated should be restricted to at least one-half potential increment (magnitude between measured values) from potential range ends for an individual polynomial fit. A flow diagram for smoothing, which employs this restriction and the condition $l = 1$, is shown in Fig. 5.

Once the data for each concentration have been smoothed, printed, punched and plotted, the adsorption parameters can be calculated.

Adsorption parameter program

The program for analyzing the smoothed capacitance data, based on eqns. (2) and (3) (version CP-I) or eqns. (4), (7) and (8) (version CP-II), performs both numerical integration and differentiation and if desired, attempts an adsorption isotherm assignment based on the computed Γ - c profiles. The procedure is outlined in Fig. 6.

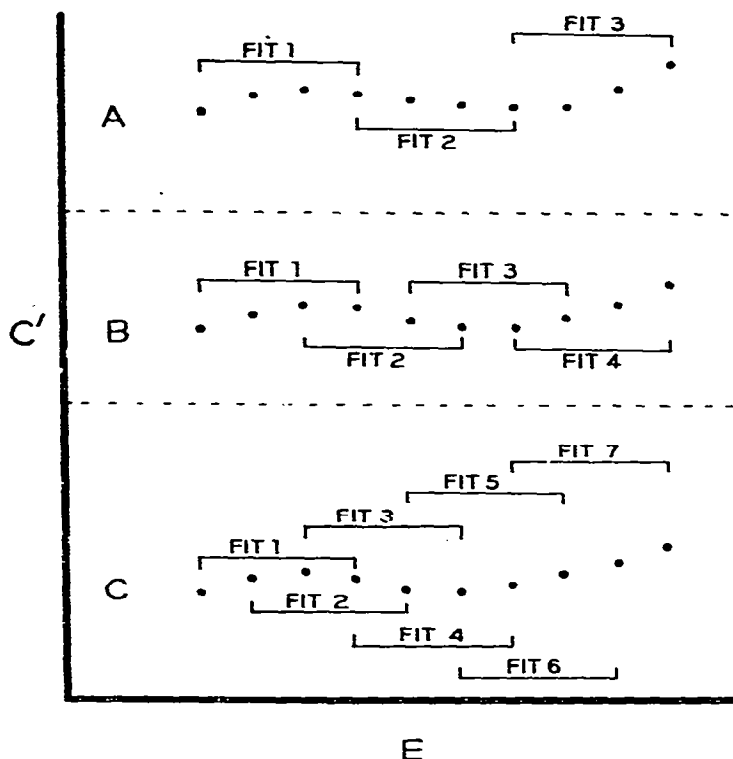


Fig. 4. Overlap of curve-fitting intervals depending on the number of points advanced for sequential fits, by using a four-point fit. A: advance three points. B: advance two points. C: advance one point.

Two alternative procedures are available for numerical integration: Simpson's Rule [17] or the least-squares technique selected which involves fitting a moving polynomial with subsequent integration of the fitted polynomial. Integration of eqn. (9) as the moving polynomial for calculation of q yields

$$\int_{E_i}^{E_{i+1}} C dE = \pi_0 (E_{i+1} - E_i) + \pi_1 ((E_{i+1}^2 - E_i^2)/2) + \pi_2 ((E_{i+1}^3 - E_i^3)/3) \quad (14)$$

whose left-hand side defines the difference in q between E_i and E_{i+1} , so that it can be rewritten as

$$q_{i+1} - q_i = \pi_0 (E_{i+1} - E_i) + \pi_1 (E_{i+1}^2 - E_i^2)/2 + \pi_2 (E_{i+1}^3 - E_i^3)/3 \quad (15)$$

The coefficients, π_1 , determined in the moving-polynomial fit of eqn. (9) are used in eqn. (15). A similar procedure is used to integrate the q - E curves to determine γ .

To minimize integration errors, a second-degree polynomial is used without smoothing. Since three points are fitted, two integrals are calculated for each fit. The polynomial is advanced one point at a time; where the

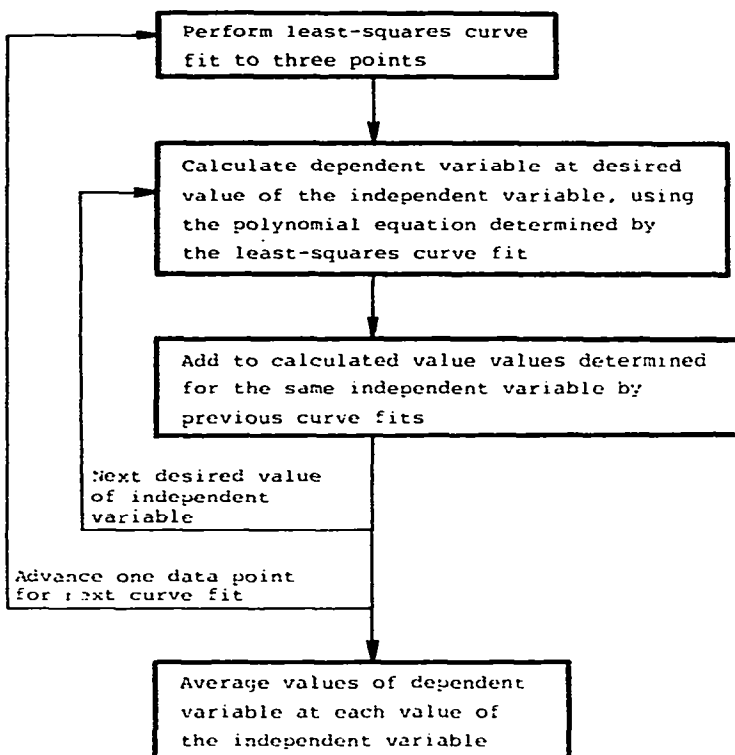


Fig. 5. Smoothing and interpolating procedure.

polynomials overlap, the integrals are averaged. Figure 7 shows a flow diagram for the integration procedure.

Starting values for q (q_1) and γ (γ_1) are required in applying eqn. (15) or the analogous equation for γ . If eqns. (2) and (3) are used, $q_1 = 0$ and $\gamma_1 = \gamma_2$. If eqns. (4), (7) and (8) are used, it is possible to use $q_1^* = 0$ and $\gamma_1^* = 0$, since the values q^* and γ^* are relative and are not concentration-dependent at E_1 .

The major difference between the method based on q and γ , and that based on q^* and γ^* , is that the latter permits integration to begin at one potential extreme, whereas the former generally requires integration to begin at a potential which is internal to the potential range. Although this is no problem with a compiler language such as PL1, it presents a problem in FORTRAN IV because data are generally stored in such an order that the corresponding potential sequentially increases or decreases. Thus, for FORTRAN IV programs, the data array to be integrated must be separated into two arrays, properly ordered for integration. It is obvious from the equation

$$\int_{E_1}^{E_i} C dE = \int_{E_1}^{E_i} C dE - \int_{E_1}^{E_1} C dE \quad (16)$$

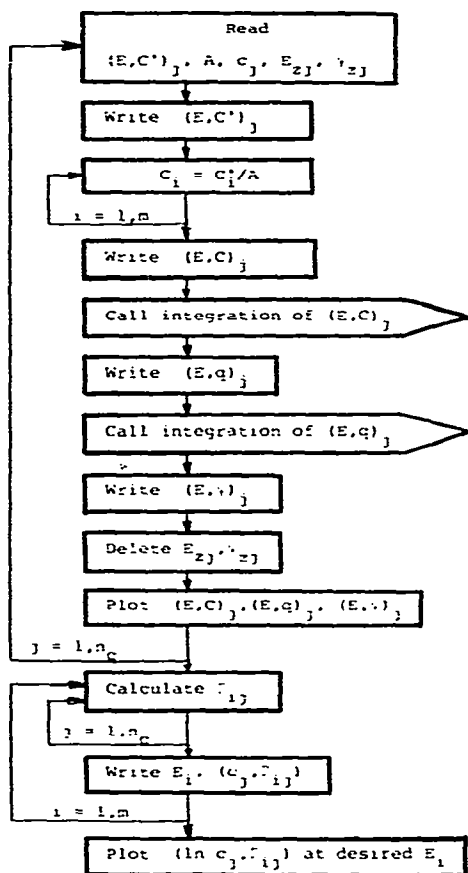


Fig. 6. Main routine procedure, where n_c is the number of concentrations and m is the number of data points per concentration.

that the method based on q^* and γ^* never requires reordering of the array. After γ or γ^* has been computed as a function of potential and concentration, the relative surface excess can be calculated, by using a moving polynomial curve fitted to eqn. (12), whose derivative is

$$\partial\gamma/\partial(\ln c) = \pi_1 + 2\pi_2 \ln c \quad (17)$$

From eqns. (11) and (17), it follows that

$$\Gamma = -(1/RT)(\pi_1 + 2\pi_2 \ln c) \quad (18)$$

For calculations based on γ^* , the negative sign in eqn. (18) is deleted. The blank data are not used in the calculations. Because eqn. (18) is a derivative of the moving polynomial equation, it is unwise to compute Γ at the edge of a fit; hence Γ is not computed for the highest and lowest substrate concentrations.

Adsorption isotherm assignment generally begins by testing for a fit to

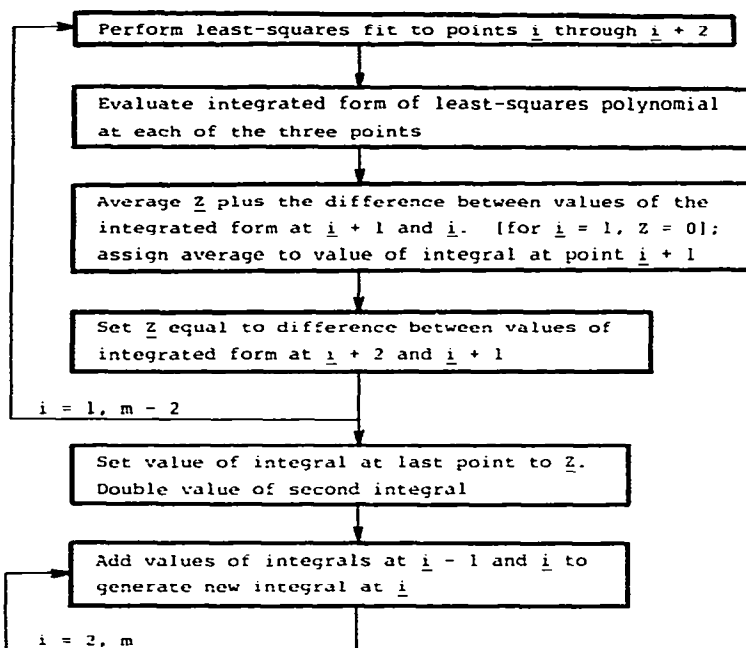


Fig. 7. Integration with the least-squares technique.

either a Langmuir isotherm (eqn. 19) or a Frumkin isotherm (eqn. 20)

$$Kc = \theta/(1 - \theta) \quad (19)$$

$$Kc = [\theta/(1 - \theta)] \exp(-2a\theta/RT) \quad (20)$$

where it is assumed that $a = c$, Γ_s is the saturation coverage, $\theta = \Gamma/\Gamma_s$, a is the interaction factor, $K = \exp(-\Delta\bar{G}^0/RT)$, and $\Delta\bar{G}^0$ is the standard free energy of adsorption. Equation (20) can be written as $K'c = \theta/(1 - \theta)$, where $K' = \exp[-(\Delta\bar{G}^0 - 2a\theta)/RT]$. The adsorption isotherm fit is made here at constant potential. Γ - c profiles are tested one potential at a time as follows: (1) supply Γ_s ; (2) calculate θ and $\theta/(1 - \theta)$ from Γ at each value of c ; (3) calculate K (hence, $\Delta\bar{G}^0$) at each c from eqn. (19); (4) check that $\Delta\bar{G}^0$ is relatively independent of c ("relatively" is defined in terms of accuracy of the data; a systematic change in $\Delta\bar{G}^0$ with c probably means that $\Delta\bar{G}^0$ is not independent of c); (5) if $\Delta\bar{G}^0$ is dependent on c , perform a linear regression on $\Delta\bar{G}^0$ vs. θ . The slope will be equal to $-2a$, and the intercept will be the "true" value of $\Delta\bar{G}^0$ for a Frumkin isotherm. Figure 8 shows a flow diagram for computing Γ and for testing for either a Langmuir or a Frumkin isotherm fit.

Surface excess at constant electrode charge

Because of the simplicity of computing Γ at constant potential, adsorption isotherm fits are made at constant electrode potential. Since there is considerable

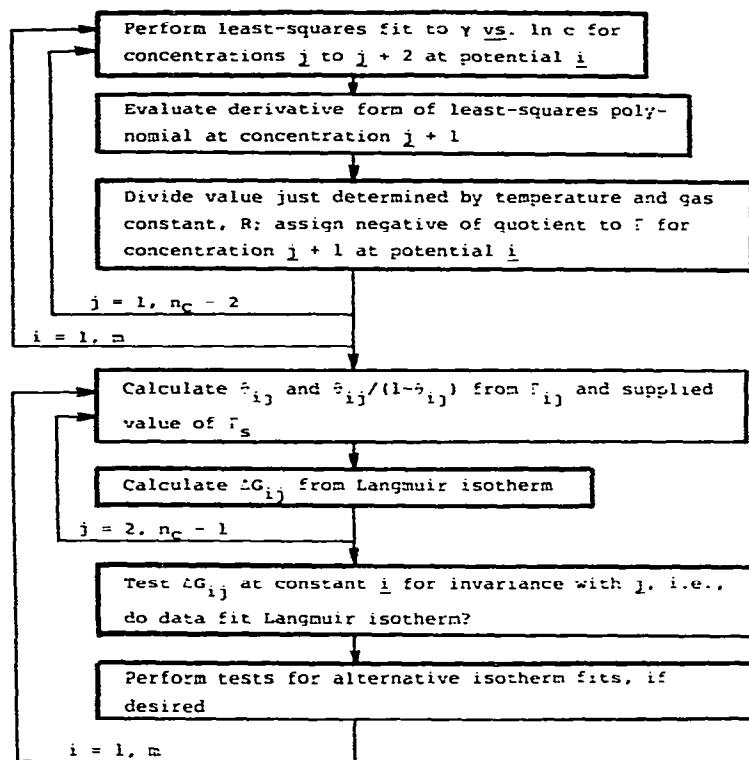


Fig. 8. Calculation of Γ at constant electrode potential and test for isotherm assignment.

controversy (cf. refs. 7 and 8) as to whether adsorption of a neutral species should show isotherm congruency at constant potential or constant charge, Γ - c profiles should be computed at constant charge and isotherm assignment under those conditions attempted.

Surface tension and charge data (available as punched output from the previous program) are supplied along with the values of q at which Γ is to be computed. The program sequentially deals with the q values; for each concentration, it scans the q - E profile to determine in what potential region q occurs. If the value of q is a data point, the corresponding value of E is noted; otherwise, a quadratic least-squares fit of q vs. E , based on eqn. (10), is performed on the three (E, q) points having values of q closest to that requested. Since eqn. (10) is a quadratic polynomial, the potential at which the desired q occurs can be calculated from

$$E = \{-\pi_1 \pm [\pi_1^2 + 4\pi_2(q - \pi_0)]^{1/2}\} / 2\pi_2 \quad (21)$$

Since there are two possible solutions for E , a test must be performed to determine which one lies within the potential range of the points fitted. For the concentration being considered and those immediately higher and lower, the γ - E profiles are scanned to find the region which includes the value of

E just determined. For each concentration, the three points (E, γ) closest to the desired E are fitted to the equation $\gamma = \pi_0 + \pi_1 E + \pi_2 E^2$; γ at the desired E is computed by interpolation for each of the three concentrations. The three points $(\gamma, \ln c)$ are used to determine Γ at the central value of c , as previously described.

Once values of Γ have been computed at all concentrations, the adsorption-isotherm tests previously described are made. Figure 9 shows a flow diagram for computing Γ at constant charge.

Charged adsorbate modification

The thermodynamic derivation for the relative surface excess of a charged species yields a relationship identical to eqn. (2), except that (1) the derivative is evaluated at constant potential versus a reference electrode reversible to the counter-ion of the charged adsorbate, or (2) a constant potential reference electrode is used and a theoretically computed correction is applied to reflect potentials referred to an electrode reversible to a solution ion.

If the adsorbate ion is sufficiently strongly adsorbed that it displaces any other adsorbed ions, which would be the usual situation of interest, the terms involving surface excesses will be negligible except that involving the adsorbate-ion of interest. If the theoretical reference electrode chosen is reversible to a supporting electrolyte-ion whose concentration remains constant as that of the adsorbate-ion is varied, the theoretical reference electrode potential is constant. Under these conditions, no potential-scale correction is required.

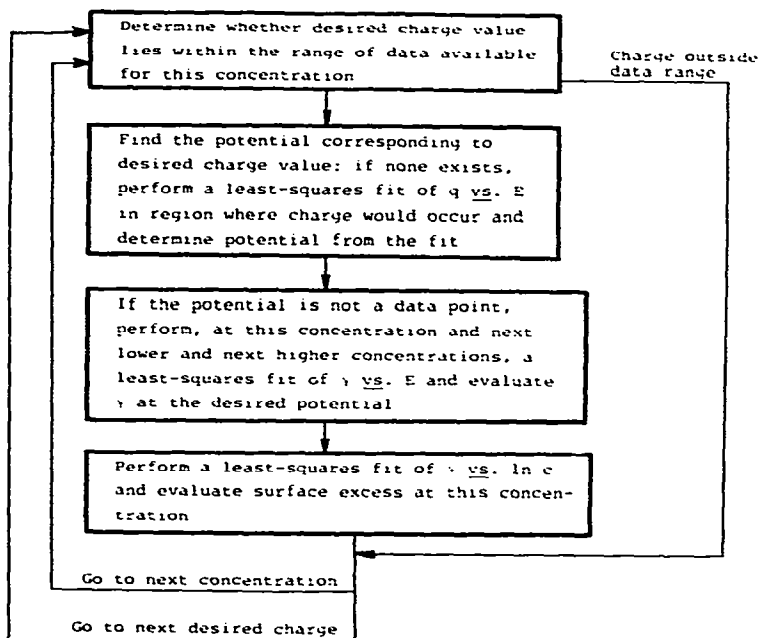


Fig. 9. Evaluation of surface excess at constant electrode charge.

Application

The experimental application of the program is discussed and the two forms of data analysis, i.e., eqns (2) and (3) (version CP-I and eqns. (4) and (8) (version CP-II), are compared in a subsequent paper [18]; the chemical system investigated is adenine in aqueous media at a dropping mercury electrode.

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REFERENCES

- 1 D. C. Grahame, *Chem. Rev.*, 41 (1947) 441.
- 2 R. Parsons, in P. Delahay and C. W. Tobias (Eds.), *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 1, Interscience, New York, 1961, pp. 1-64.
- 3 P. Delahay, *Double Layer and Electrode Kinetics*, Interscience, New York, 1965.
- 4 D. M. Mohilner, in A. J. Bard (Ed.), *Electroanalytical Chemistry*, Vol. 1, Marcel Dekker, New York, 1966, pp. 241-409.
- 5 E. Gileadi, (Ed.), *Electrosorption*, Plenum Press, New York, 1967.
- 6 C. A. Barlow, Jr., in H. Eyring, D. Henderson and W. Jost (Eds.), *Physical Chemistry - An Advanced Treatise*, Vol. IXA, Academic Press, New York, 1970, pp. 167-246.
- 7 R. Parsons, *Pure Appl. Chem.*, 18 (1968) 91.
- 8 R. Payne, *J. Electroanal. Chem.*, 41 (1973) 277.
- 9 H. H. Bauer, P. J. Herman and P. J. Elving, in J. O'M. Bockris and B. E. Conway (Eds.), *Modern Aspects of Electrochemistry*, Vol. 7, Plenum Press, New York, 1972, pp. 143-197.
- 10 A. N. Frumkin and B. B. Damaskin, in J. O'M. Bockris and B. E. Conway (Eds.), *Modern Aspects of Electrochemistry*, Vol. 3, Butterworths, London, 1964, pp. 149-223.
- 11 B. B. Damaskin, O. A. Petrii and V. V. Batrakov, *Adsorption of Organic Compounds on Electrodes*, Plenum Press, New York, 1971.
- 12 S. Trasatti, *J. Electroanal. Chem.*, 53 (1974) 335.
- 13 R. S. Perkins and T. N. Anderson, in J. O'M. Bockris and B. E. Conway (Eds.), *Modern Aspects of Electrochemistry*, Vol. 5, Plenum Press, New York, 1969, pp. 203-290.
- 14 P. R. Mohilner and D. M. Mohilner, in J. S. Mattson, H. B. Mark, Jr. and H. C. MacDonald, Jr. (Eds.), *Electrochemistry*, Marcel Dekker, New York, 1972, pp. 3-44.
- 15 H. C. MacDonald, in J. S. Mattson, H. B. Mark, Jr. and H. C. MacDonald, Jr. (Eds.), *Electrochemistry*, Marcel Dekker, New York, 1972, pp. 45-59; H. C. MacDonald, Ph.D. Thesis, The University of Michigan, Ann Arbor, 1969.
- 16 D. C. Grahame, E. M. Coffin, J. I. Cummings and M. A. Poth, *J. Am. Chem. Soc.*, 74 (1952) 1207.
- 17 D. G. Moursund and C. S. Duris, *Elementary Theory and Application of Numerical Analysis*, McGraw-Hill, New York, 1967.
- 18 M. Katz, T. E. Cummings and P. J. Elving, submitted for publication.