Tensammetry:

Review of Literature and Results of Initial Experiments

for

The Adsorption of Surfactants

A Research Project Sponsored by

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475 Park Avenue South

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by

Fred B. Rea and John C. Westall

Department of Chemistry
Oregon State University
Corvallis, Oregon 97331-4003
(503) 754-2591

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INTRODUCTION

Here we present a brief overview of our work on tensammetry for the determination of the activity of surfactants in solution. This report consists of two parts:

Review of literature
Results of initial experiments

We have not included in this report a thorough description of just how tensammetry works. For those unfamiliar with tensammetry, we recommend reading the literature review, skimming the titles of the references, and then skimming the results section, checking the calibration curves (e.g., Figure 7) and the kinetics (e.g. Figure 3). There will be an opportunity to discuss tensammetry in detail at the meeting in New York at the end of March.

We are optimistic about the application of tensammetry to problems of environmental chemistry. Considerable progress has already been made in this direction by Cosovic and co-workers.

A survey of the literature concerning tensammetry was undertaken to answer several questions. The apparatus and methods in use in other laboratories were of primary interest. Also of specific interest is the experimental data best suited to quantitative analysis.

Instrumentation

The instruments in use by various research groups are summarized in Table 1. Specific attention was paid to the potentiostat, as its speed is a primary limiting factor in the success of the technique.

Table 1. The breakdown of potentiostats in use is as follows:

Instrument[1]	Number in use
"Homemade"	5
PAR 174A[2]	4
PAR 170	2
Radelkis OH105	2
Miscellaneous	1 each
BAS LC-4	
GWP 563 (Deutsche Akademie der Wissenschaften)	
Metrohm E261/E393	
Metrohm E506	
PAR 173/179[3]	
Unitra PP04	

Notes:

1 In most, but not all, cases the apparatus is controlled with a computer.

2 In cases where the PAR 174A is used, the instrument has been altered to allow an external signal to be added at the summing point of the main potentiostat.

3 Although not tensammetry, similar kinds of measurements were performed with a PAR 173/179 (Hindagolla,1985)

Chemical purity

All authors took some measures to ensure the purity of blanks, with widely varying degrees of concern over sample cleanliness. The major materials of note were water, mercury, purging gas, and supporting electrolyte.

The widest variance in purity assurance was found in treatment of water. One group (Bednarkiewicz, 1981) did an extensive study of several methods of water purification, from doubly distilling tap water to a lengthy process involving multiple distillations at atmospheric and reduced pressures, Amberlite XAO2 filtration, and activated charcoal filtration. Most other authors used twice- or thrice-quartz distilled water, with two exceptions. Hunter (1981) irradiated supporting electrolytes and solvents with UV light to remove organics, and Bos (1982) used water from a Millipore Q2 system.

Nearly all authors used triple distilled polarography grade mercury. Cosovic indicated the use of only double distilled mercury, and Gupta (1965) washed, filtered, and vacuum distilled his own.

Most authors used N_2 purging of samples to remove O_2. Those who specified N_2 purity indicated high quality or ultrapure N_2. Bos (1982) took the additional precaution of passing his N_2 through copper tubing at 450 C. Bednarkiewicz (1985) purged his solutions with argon, and Cosovic (1972) commented that better results were obtained for some samples if no purging was done.

Some variation in supporting electrolyte purity requirements was found. Bednarkiewicz (1985) and Cosovic (1982) purified some supporting electrolytes with activated charcoal. In addition, Cosovic (1977,1982) baked NaCl at 450 C for several hours. Pawlak (1987) purified Na_2SO_4 by double recrystallization and subsequent heating at 600 C. Most other authors specified reagent or analytical grade electrolytes.

An additional procedural precaution was temperature control. Two authors indicated work was done at 20±1 C and another preferred 25.0 C. Cosovic indicated that experiments were performed at room temperature without thermostatic control. Over half of the authors cited did not specify any temperature control precautions.

Experimental measurements

A general tensammetric experiment involves application of a changing potential to a hanging or dropping mercury electrode and processing the measuring the output current to determine the double layer capacitance. The specific method of tensammetry is characterized by waveform of the applied potential. The most popular techniques fall into two major categories: ac tensammetry and differential pulse tensammetry.

AC tensammetry employs a small sinusoidal potential superimposed on a DC ramp as the applied potential. The quantity measured is the ac amplitude of the cell current. This is achieved with a lock-in amplifier in some cases. In others, the buffered ac current is rectified and the rms amplitude measured directly with a voltmeter. One author (Gupta,1965) measured the amplitude at discrete points with an oscilloscope. AC tensammetry may be further categorized by the relation between the excitation frequency and the measurement frequency, in cases where a lock-in amplifier is used.

The most common tensammetric method is ac fundamental tensammetry (acft). Here the cell current is monitored with a lock-in amplifier or a phase nulling device tuned to the fundamental ac frequency. This method is prone to having large background, due to background Faradic processes.

The large background of ACFT may be avoided with ac second harmonic tensammetry (acsht). Here the reference signal for detection has a frequency twice that of the excitation waveform. The major advantage of this method is its low background current. A Faradic process will be responding to the applied potential at any given moment, and will therefor have a vanishingly small second harmonic contribution. The capacity current, however, will have a second harmonic component. The primary disadvantage of acsht is the small magnitude of the second harmonic signal. This need not be a major limitation, however, as many lock-in amplifiers are capable of isolating and measuring sinusoidal signals with amplitudes in the microvolt range.

Differential pulse tensammetry (dpt), is actually a collective term for several techniques which employ applied potential waveforms other than a sinusoid. These methods may be used in a single drop (HMDE) mode or with a DME. Some authors employing this technique are using simple DP polarographs with little or no modification. Others, most notably Cosovic, are using a waveform generator known as a Kalousek commutator. Here the applied potential is mechanically chopped between a linear ramp and a constant potential, usually the electrocapillary maximum potential, E_z. Some authors are working with differential step waveforms (as in square wave voltammetry), due to the ease with these forms may be digitally generated. In all cases, the DC current is sampled after a discontinuous change in the applied potential. In the absence of Faradic processes, the DC current is due only to charging of the double layer.

<u>Interpretation</u> <u>of</u> <u>data</u>

The data obtained by either method is a curve of differential capacitance as a function of applied dc potential. In pure supporting electrolyte this curve generally exhibits a single broad peak. The maximum of this peak, the electrocapillary maximum, is at the point of zero surface charge on the mercury drop; its potential is designated E_z. In the presence of a surface active substance, the curve of differential capacity versus applied potential displays two peaks separated by a trough. One peak is at a potential more negative than E_z and is designated s^-. The other peak, at a potential more positive than E_z, is designated s^+. The broad peak due to the supporting electrolyte is generally not observed in the presence of surface active substances.

Ideally the parameter selected for quantitative analysis would have a relatively large region of a linear dependence on concentration and would be readily and reproducibly obtainable from the raw experimental data. The position (E_s-, E_s+) and height ($C(E_s-)$, $C(E_s+)$) of the desorption peaks and the magnitude of the capacitance at E_z exhibit some dependence on the bulk activity of surface active substances in the solution. The s^- and s^+ peaks increase in amplitude and separation from E_z with increasing bulk concentration. The ac current at E_z decreases with increasing bulk concentration. All five of these quantities are readily available from the experimental data.

Measurements on the electrocapillary maximum are normally done as suppression of i_{ac} at E_z from the blank (supporting electrolyte). Bednarkiewicz (1981) indicated a linear relationship between the suppression of the ac current at E_z and the surfactant concentration. Ulrich (1986,1988) derives a more complex relationship between i_{ac} at E_z and C through considerations of thermodynamic treatment of surface coverages. The total capacitance, C_T, at low values of the surface coverage fraction   is:

$$C_T = C_R \quad + C_0(1 - \quad)$$

where C_R is the capacitance of the mercury surface with a monolayer of a surfactant R and C_0 is the capacitance of the surface with only supporting electrolyte and solvent adsorbed.

The s^+ peak is not considered by most authors. The scan normally begins at a potential more positive than E_s+ and proceeds in a negative direction. Since the surface active substance does not adsorb significantly at potentials more positive than E_s+, observation of a clear s^+ peak is rare and not expected. A notable exception is Britz (1981), who was working in low ionic strengths (0.05 <u>M</u>). Bednarkiewicz (1981) managed to produce data for this peak by performing the tensammetric scan in two segments -- one scan toward E_s- from a rest potential near E_z and then a separate scan toward E_s+, again from near E_z. The difficulty in reproducibly observing the s^+ peak led him to use current suppression at E_z as his quantitative signal.

The s^- peak is the third possible point of analytical interest. This peak is generally well-resolved from others, and its height and position have both been used as analytical signals. According to Britz (1980), i_{s-} is more linear at low concentrations, while E_{s-} is preferable when concentrations are higher.

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Apparatus

The apparatus for tensammetric analysis consists of a potentiostat, a current-to-voltage convertor, a digital voltmeter, a lock-in amplifier, an electrochemical cell, and a computer.

The potentiostat and current-to-voltage convertor are both housed in an IBM EC/225 Voltammetric Analyzer. Its potentiostat and current-to-voltage convertor are both fast enough to allow use of ac frequencies up to 500 Hz. The current to voltage convertor output is directed to the input of the lock-in amplifier.

The applied potential from the EC/225 is measured with the Keithley Model 617 Programmable Electrometer. This provides a digital signal to the computer, as the only outputs from the EC/225 are analog.

The PAR 5301 Lock-In Amplifier serves both as the source of the ac signal and the detector for the ac current amplitude. The internal oscillator of the 5301 is set to 105 Hz at 30 mV peak to peak amplitude. The oscillator output is sent into the auxiliary input of the IBM EC/225.

The computer, a Cordata PPC-400, is interfaced to the Keithley 617, the PAR 5301, and the IBM EC/225. The Keithley 617 and the PAR 5301 interface is a National Instruments GPIB-PCIIA card. The EC/225 is controlled via a MetraByte PIO12 Parallel Interface card.

The analog data are recorded on a Heath Model SR-207 X-Y recorder. The traces from the X-Y recorder are used primarily for diagnostic purposes. All numerical data are taken from the digital record.

The electrochemical cell is the PAR Model 303 Static Mercury Drop Electrode equipped with a borosilicate glass sample cup. A Model 305 Stirrer is also used. The PAR 303 is used in three-electrode mode, with a Ag|AgCl reference electrode.

Procedure

The cell and all glassware are cleaned with HPLC grade methanol acidified with 10^{-2} M HCl.

Solutions are prepared from water freshly delivered from a Millipore Milli-Q Q2 system. The specific resistance of the water does not drop below 17 Mohm•cm. Stock solutions are refrigerated at 4 C when not in use.

Each sample solution is prepared individually in a 10-mL volumetric flask. A constant concentration of the supporting electrolyte is maintained in all solutions. The desired concentration of a surface active substance is prepared by transferring by Eppendorf pipet a stock solution (with supporting electrolyte) into the 10-mL flask and diluting with supporting electrolyte.

The contents of the volumetric flask are transferred to the PAR 303 sample cup, which is fitted into position. The solenoid in the 303 which controls the flow of purging gas is actuated from the computer, allowing a purge time of 10 minutes, rather than the maximum of 4 minutes available from the 303 front panel.

The purging gas is standard grade nitrogen which is passed through a vanadous chloride scrubber to remove oxygen. A bubbler of the supporting electrolyte downstream of the vanadous chloride scrubber protects the cell from any carryover from the scrubber.

The initial potential of the EC/225 sweep is set to E_z, the electrocapillary maximum as determined from a run of supporting electrolyte alone. Two drops are extruded end dislodged from the electrode. A third drop is extruded but not dislodged. With the stirrer running, a predetermined accumulation time is allowed to pass before initiation of the scan.

After the accumulation time has passed, the scan toward positive potentials is initiated. The dc scan rate is 10 $mV \bullet s^{-1}$. The dc potential is monitored, and the scan is reset when the potential reaches -0.1 V vs. Ag|AgCl. Three more drops are extruded, the third of which is retained for the accumulation and scan in the negative direction. The negative scan is terminated at a potential of -1.3 V vs. Ag|AgCl.

Results

Figure 1 shows the tensammogram of a 1 M Na_2SO_4 blank. Accumulation conditions were 60 s at -0.6 V vs. Ag|AgCl. Note that the potential axis is -E(dc), with negative values on the right. The E_z estimated from this curve is -0.25 V.

Figure 2 shows the tensammogram of $1x10^{-5}$ $\underline{M}$ 1-dodecylpyridinium bromide (C_{12}PYR) in 1 $\underline{M}$ Na_2SO_4. The accumulation time was 60 s, and the accumulation potential was -0.6 V vs. Ag|AgCl. The large peak at -60 mV is the s^+ peak, and the smaller feature at -1.25 V is the s^- peak. The magnitude of i(aqc) at -0.25 V is interpolated from the data to give the suppression at E_z.

It has been found that, at low concentrations of surfactants, it is sometimes difficult to achieve reproducible results from ostensibly identical conditions. The variability has been attributed to variable adsorption on the walls of the cell, resulting from variable pretreatments of the cell. Normally three or four pre-equilibrations are sufficient to get reproducible scans at concentrations as low as 0.1 $\underline{M}$.

Figure 3 shows the decrease in the ac component of the cell current at constant potential with time. The sample solution is C_{12}PYR in 1 $\underline{M}$ Na_2SO_4. The four curves correspond to bulk concentrations of 100, 10, 1, and 0.1 $\underline{M}$. Figure 4 shows the analogous curves for sodium 4[(2'-dodecyl)benzene] sulfonate (C_{12}LAS) in 0.1 M KNO_3. Due to the difficulty in working at low concentrations of C_{12}LAS, no 10^{-7} M curve is shown in Figure 4.

The surface concentration, calculated from the ac suppression at E_z, has been plotted against bulk concentration for C_{12}PYR in Figures 5 through 7. Figure 5 covers the entire range of concentrations in the experiment. Figure 6 is a more detailed look at the lower concentration range. Figure 7 is a plot of the same data on a log concentration scale.

Figure 8 shows the data taken so far for C_{12}LAS in 0.1 M KNO_3. Again, difficulty in obtaining reproducible results at low concentrations has slowed extension of C_{12}LAS work into sub-micromolar concentrations.

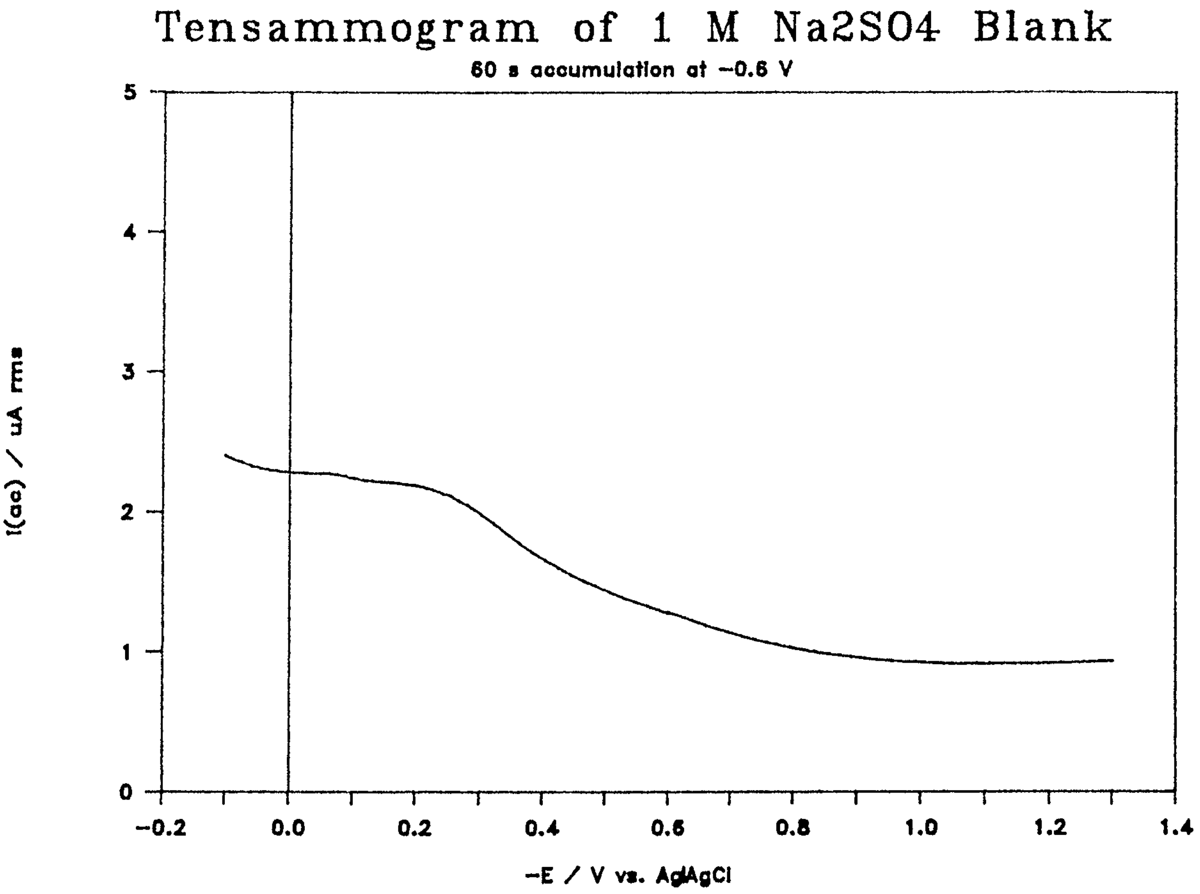

Figure 1. Tensammogram of 1 M Na_2SO_4 blank.

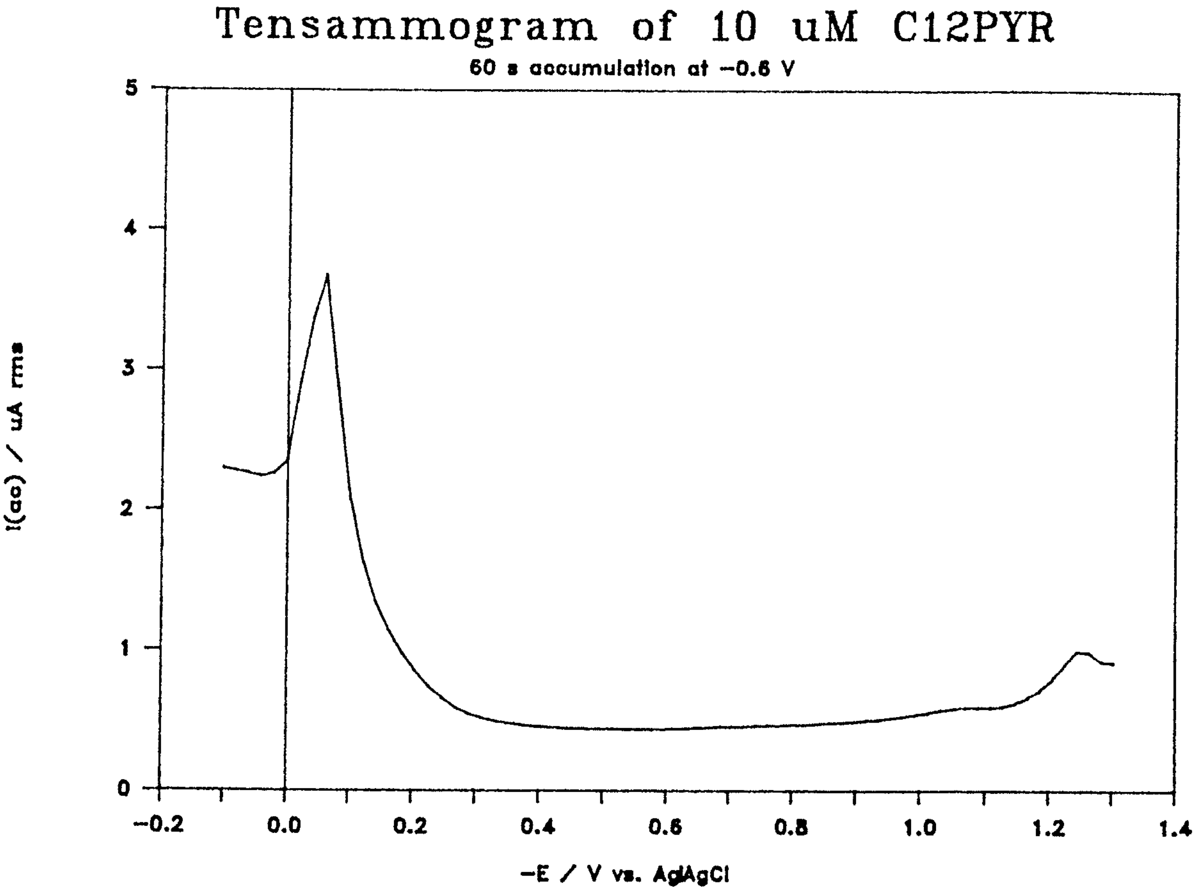

Figure 2. Tensammogram of 1×10^{-5} $\underline{M}$ $C_{12}PYR$ in 1 $\underline{M}$ Na_2SO_4.

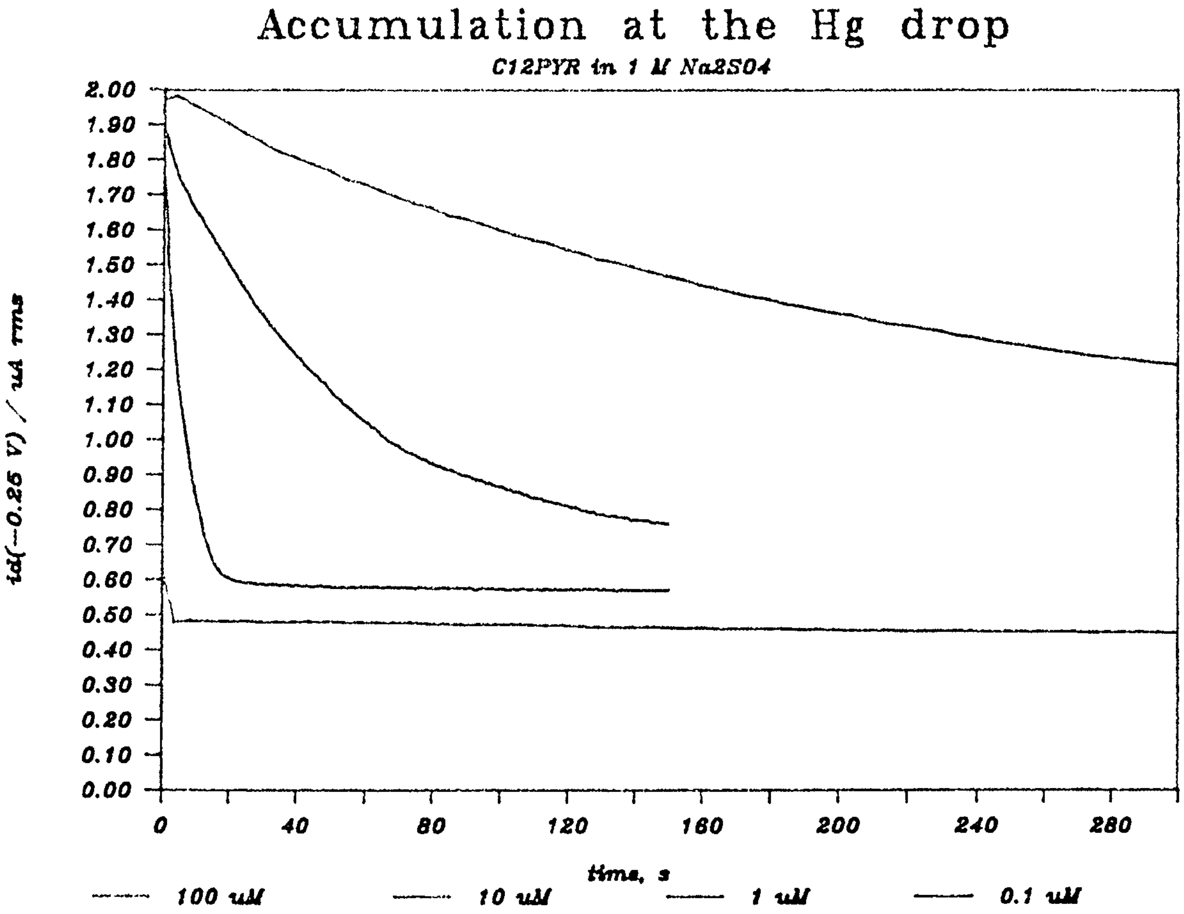

Figure 3. Kinetics of C_{12}PYR adsorption on the mercury drop. The lowest curve corresponds to 100 μM C_{12}PYR. The supporting electrolyte is 1 M Na_2SO_4.

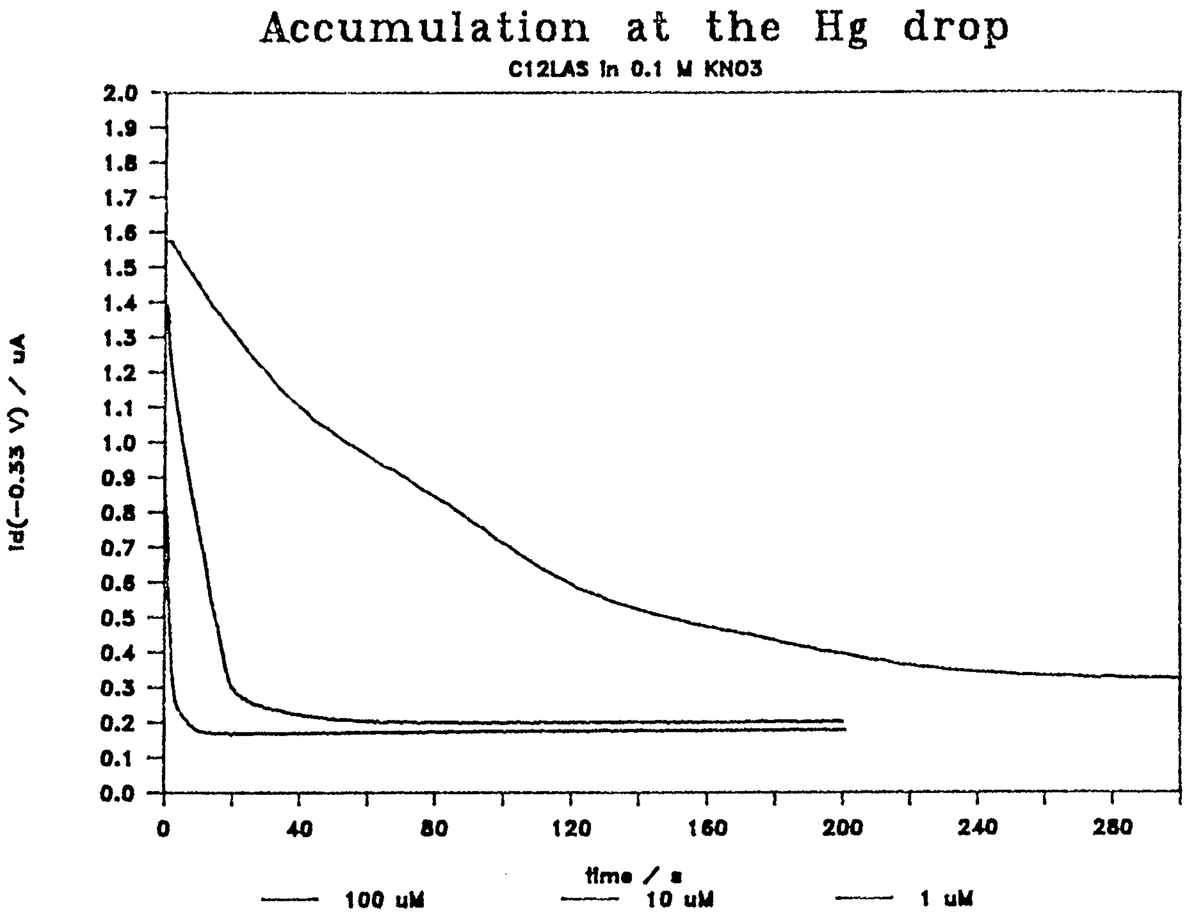

Figure 4. Kinetics of C_{12}LAS adsorption on the mercury drop. The lowest curve corresponds to 100 $\mu\underline{M}$ C_{12}LAS. The supporting electrolyte is 0.1 M KNO_3.

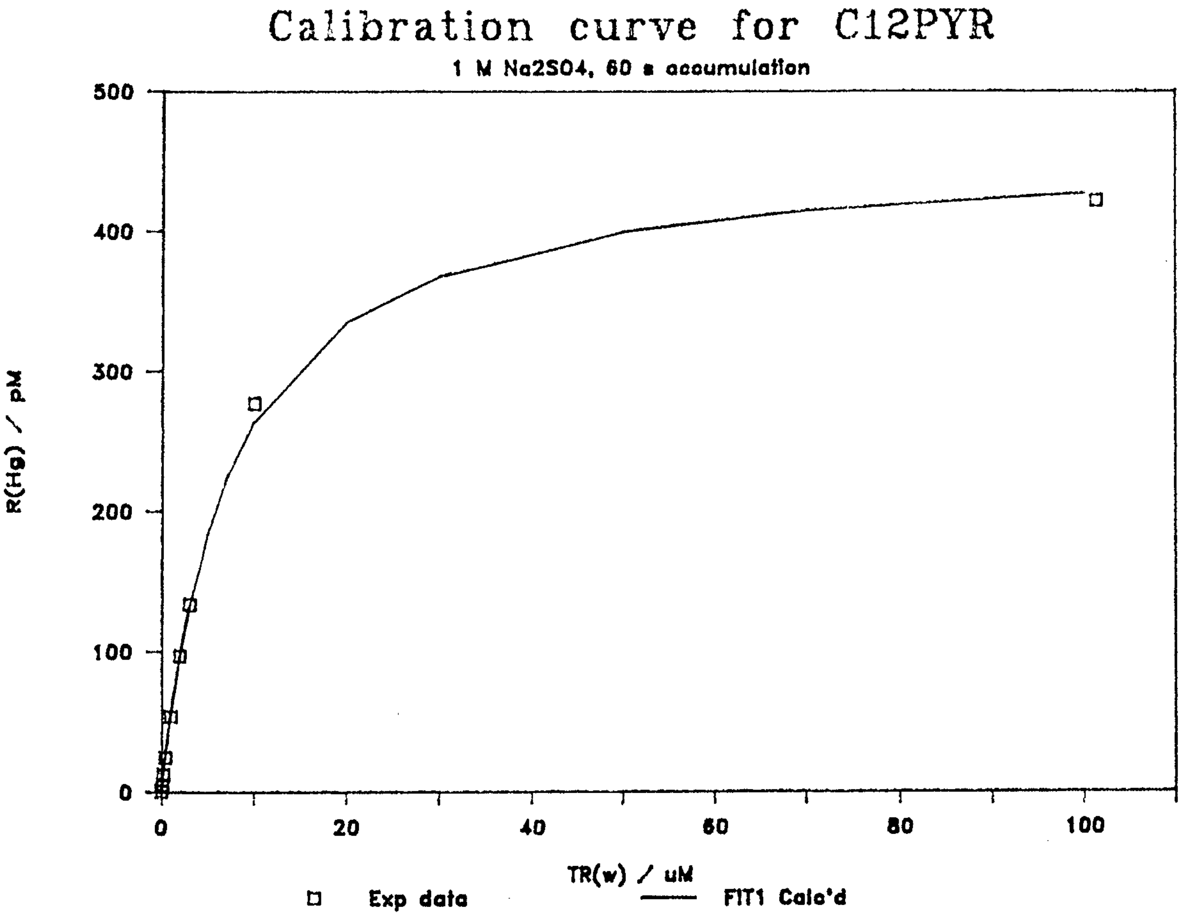

Figure 5. Calibration curve for $C_{12}PYR$. The curve is calculated from FITEQL version 1.2.

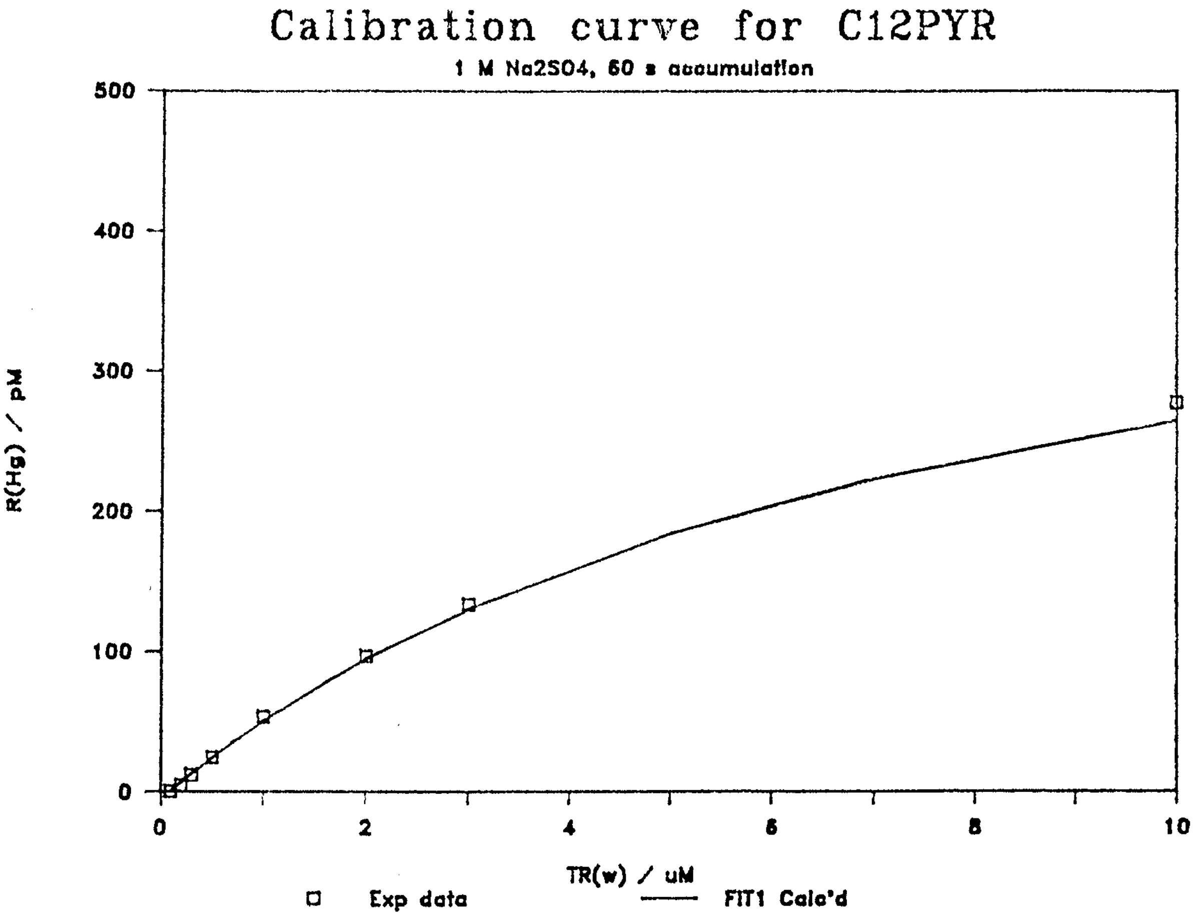

Figure 6. Expanded calibration curve for C_{12}PYR.

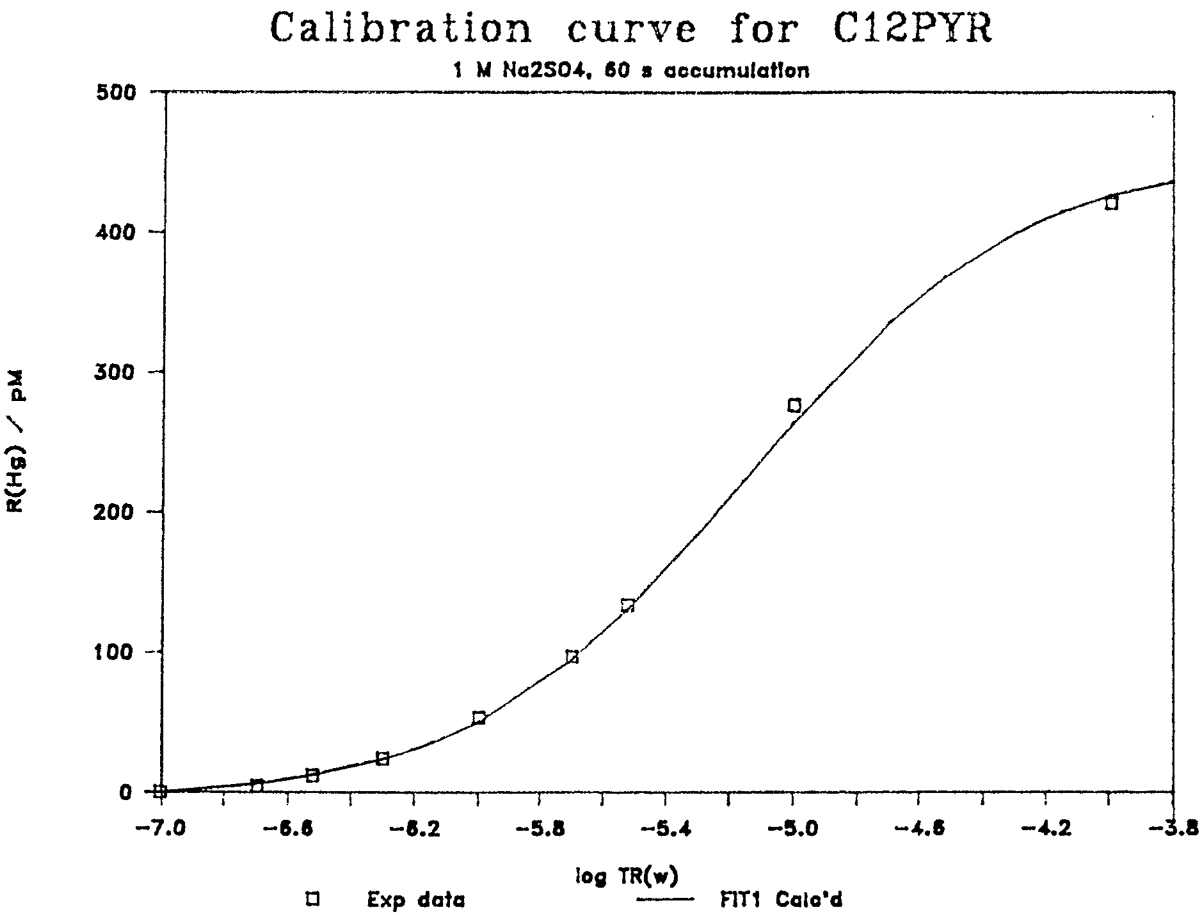

Figure 7. Calibration curve for C_{12}PYR with log concentration scale.

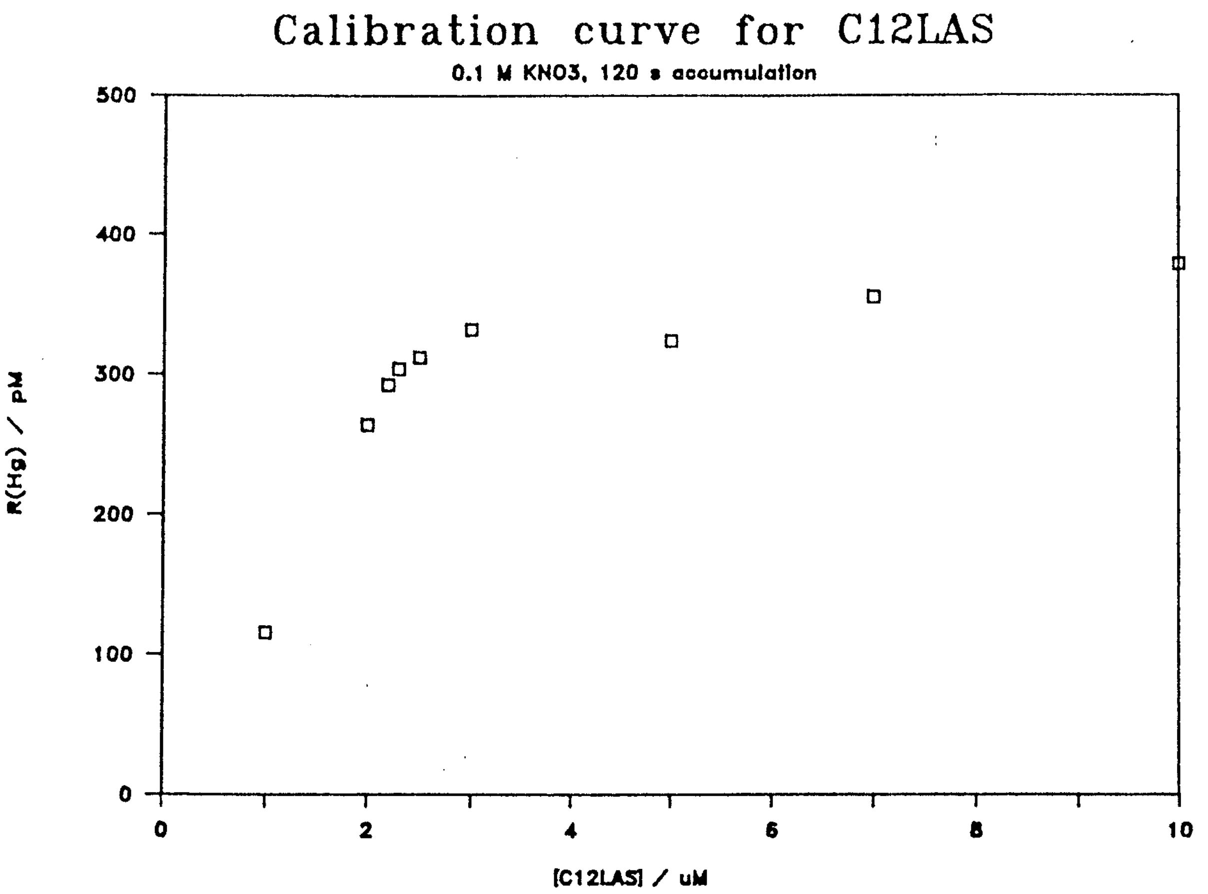

Figure 8. Calibration curve for C_{12}LAS. The scale is the same as that of Figure 5 for comparison.