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ON THE ADMITTANCE OF THE NEEDLE PEAK

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ON THE ADMITTANCE OF THE NEEDLE PEAK

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Abstract

We respond to recent criticism (R. D. Armstrong, J. Electroanal. Chem., 372 (1994) 27) of our earlier paper on the admittance of the needle peak of tetrabutyl ammonium bromide at the mercury-water interface (J. Electroanal. Chem., 352 (1993) 279), and pinpoint areas of serious misunderstanding.

In a series of papers [1-3] we have reported on the adsorption behavior of tetrabutylammonium ions at the mercury-water interface, a system studied earlier by a variety of workers. (For extensive references to those earlier studies see [1]). The third of these papers examined the admittance of the so-called needle peak, a sharp and narrow capacitance peak, which was first reported by Frumkin et al. [4]. We presented experimental results, and a theoretical model that qualitatively explains the main features of these results [3]. In a recent communication [5], Dr. Armstrong takes issue with the adequacy of the data we reported, and with the validity of our theoretical model. Both the substance and vehemence of his objections require that we reply to Dr. Armstrong's comments.

In his comments [5], Dr. Armstrong purports to show that the impedance we have reported "is not the normal well-defined small amplitude electrode impedance", and that our model "is at variance with standard nucleation theory". Below we will address both aspects. Some outright thermodynamic errors in [5], such as the statement that the charge density exhibits a Dirac delta function at the transition potential, we will just leave to the reader to judge. Instead we will try to focus on some of the more substantial issues involved.

A well-known rhetoric device, albeit of doubtful scientific value, is to force an issue in terms of a binary question, without leaving space for viable alternatives. Such is the case with the question Dr. Armstrong poses regarding the discontinuous or continuous transition. Dr. Armstrong assumes that, in the case of the needle peak of tetrabutyl ammonium bromide [3], there are just two possibilities: either we have no phase transition, but merely a desad peak of the type analyzed by Melik-Gaikazyan & Frumkin [6] and Lorenz & Möckel [7], or we have a phase transition, in which case it is presumed to be discontinuous. There are two separate questions here: whether or not we deal with a phase transition and, if so, whether that phase transition is continuous or discontinuous. In our case, the needle peak is clearly associated with a phase transition, and our experimental data (as well as those of others) suggest that such a transition may allow for a coexistence region, in which case there exists a continuous path from the noncondensed to the condensed state and vice versa. The question Dr. Armstrong poses is a fallaceous one.

It is, likewise, dangerous to argue by analogy, such as an analogy with the phase transition between a gas and liquid phase, especially when that phase transition involves bulk phases and, therefore, has a dimensionality different from that considered here. For example, a spherical water droplet can only communicate with its surroundings through its surface, whereas a circle in a plane separating two bulk phases can communicate with one of the bulk phases through its surface area, and with the adsorbate in the interface through its periphery. This peculiarity of the two-dimensional system was, in fact, one of the major features of our analysis, as it also was in a more recent study by Schrettenbrunner et al. [8]. In the introduction to our paper [3] we specifically alerted the reader to the difference in dimensionality, and to its consequences.

The dependence on amplitude

Dr. Armstrong states that our admittance either must be amplitude-dependent, or fit the Lorenz & Möckel equation. As with the previous point, this is a false dilemma, and the answer is "neither". Dr. Armstrong then goes on to ask rhetorically whether there was a variation of the impedance with amplitude, even though he already knows (from our unpublished data, to which he was privy, and from which he quotes) that the answer to this question is an unambiguous "no". Likewise, the answer to his question about a possible fit of our experimental data to the Lorenz & Möckel model can be found merely by inspection of Figs. 4 and 5 in ref. [3]. Again, the answer is obviously "no".

As can be seen in Fig. 1, the admittance at the needle peak is the same regardless of whether we use an amplitude of 0.25 mV, of 0.5 mV, or of 1.0 mV. Only at larger amplitudes than used here will the sinusoidal current no longer be directly proportional to the amplitude of the sinusoidal signal used. Fig. 2 shows the absolute magnitude of the same admittance as an explicit function of frequency, again for the various amplitudes used. At amplitudes below those used here, the low-frequency data become too noisy to be of much use. Figure 2 also contains the harmonic response, which is relatively small. At frequencies above about 10 Hz, the harmonic response is dominated by noise. At lower frequencies, the harmonic response exhibits the expected proportionality of the current at the double frequency, $i_{2\omega}$, with the square of the voltage amplitude ΔE. The presence of a harmonic response is, of course, quite common in electrochemical measurements, and results from the non-linear behavior of the system. The important point here is that the magnitude of the harmonic current is small compared to that of the fundamental current, thereby experimentally justifying truncation of the Taylor series expansions in deriving a model for the admittance.

Figs. 1,2

The width of the needle peak

How small should the amplitude be in order to yield a reliable electrode admittance ? While the approach described in the preceding paragraph verifies that we indeed have used a sufficiently small amplitude, another answer to that question can be obtained by directly measuring the width of the needle peak. Figure 3 illustrates capacitance-potential curves measured with a scan rate of 1.0 mV s^{-1} at 20 Hz, using two different amplitudes, 0.5 and 0.25 mV. It is again clear that the curves are independent of the amplitude of the alternating voltage used. Moreover, the curves contain capacitance values determined from potential step experiments such as shown in Figs. 4 and 5 (see below) but using 20 Hz and measured 100 s after the step, i.e., well after the transients have died out.

Fig. 3

Fig. 3 shows a peak width at half height of about 2.5 mV. It would be ideal to have measurements with amplitudes of no more than a few percent of this width at half height, but the noise in our potentiostat and the problems associated with measuring subHertz admittances with small amplitudes make this difficult. Still, an amplitude of 0.25 mV for a peak width of 2.5 mV should be adequate to yield results relatively free of distortion.

The fact that the peak is considerably wider than the amplitude of the sinusoidal voltage used to probe it is significant in another way. It clearly demonstrates that we are not dealing here with a discontinuity in the capacitance-potential plot, merely broadened by the signal used to sample it, but that the observed needle peak has a non-zero width independent of the measurement method used. Whether this is an inherent width, or is due to some unidentified inhomogeneity in our electrochemical system, cannot be ascertained at present.

We prefer the above criteria (independence of the measured admittance to significant changes in voltage amplitude used, and relatively small harmonic content) to the rather arbitrary or simply incorrect criteria listed by Dr. Armstrong, such as requiring that the charge density vary by less than 1% of its time-averaged value. This would invalidate, e.g., all capacitive determinations of the potential of zero charge in dilute solutions.

The existence of a steady state

Dr. Armstrong questions whether our experiments are steady-state experiments. Clearly, it would not have been possible to make the admittance measurements we reported earlier [3], which took at least a half hour to complete per frequency run, had there not been a condition of steady state. In general, we can "ride" the needle peak for hours, as long as the mercury droplet doesn't fall, and with periodic minor adjustments of the potential, by fractions of a millivolt, to correct for potentiostat drift.

We earlier reported [2] single potential step experiments in which, starting from within the pit region, we jumped to various potentials approaching the pit edge. In such experiments (e.g., Fig. 12b of ref. 2) the capacitance dwells longer at the needle capacitance the closer one approaches the potential of the needle peak, and the same applies when we approach the potential of the needle peak from the other side (ref. 2 Fig. 13b). In Figs. 4 and 5 we report additional experimental evidence attesting to the stability of this steady state when approached from either side. The frequency used in these measurements is much higher than the reciprocal of the characteristic times of the transients used, so that the alternating signal does not distort the measured phenomenon, and vice versa.

Figs. 4,5

In the double potential step experiments of Fig. 6 we show that the same steady state is reached whether we step directly from outside the pit to the center of the needle peak, or purposely overshoot the needle peak and dwell for some time inside the pit region. It is likely that, in experiments stepping directly from outside the pit to the peak potential, nucleation has resulted from a brief overshoot of the potential within the first millisecond after the step. In experiments in which the potential is scanned slowly, the needle peak is often observed only when one scans from inside to outside the pit region, even when the hysteresis region is very narrow [9]. This clearly indicates that, for the needle peak to be observable, clusters must be present.

Fig. 6

Experimental details

Since the admittance measurements reported earlier [3] were made with a borrowed frequency response analyzer, which has long since been returned to its owners, we have repeated these measurements with another frequency response analyzer, a Solartron model 1250 kindly loaned to us by Dr. R. E. Ricker of the National Institutes of Standards and Technology in Gaithersburg, MD. The data displayed in Figs. 1 and 2 were obtained with this instrument. We used a Stanford Research Systems model 830 digital lock-in amplifier to record the capacitance-potential and capacitance-time curves shown in Figs. 3 through 6. In all other respects, the equipment was as described earlier [3]; specifically, the same mercury drop dispenser, measurement cell and potentiostat were used. All experiments apply to mercury droplets of 2.37_5 mm^2 area in contact with an aqueous solution of 3 mM tetrabutylammonium bromide (TBABr) in 0.5 M NaBr at 5^oC. As before, all potentials were measured versus an external saturated calomel electrode.

Theoretical results

The second type of criticism of our work concerns the theoretical interpretation of our experiments. Dr. Armstrong argues that our interpretation somehow violates standard nucleation theory. This is an interesting charge considering that, in our model, we claim an absence of nucleation during the observation period. Of course, there must have been nucleation *prior* to achieving the steady state, because clusters must be present. However, during the ensuing steady state, no additional clusters are nucleated, which is why nucleation as such does not enter our model.

Dr. Armstrong admonishes us that our starting equation, eqn.(1) of ref. [3], includes "no term which relates to the edge Gibbs energy of the nucleus". This is a mystifying comment: kinetic expressions should only contain *activation* free energies, not *equilibrium* free energies such as the edge energy. At any rate, by using different rate constants for molecules at the cluster edge and for those at the cluster surface we explicitly account for the special nature of the cluster edge in our model. Similarly puzzling is Dr. Armstrong's assertion that we "only allow kinetically hindered adsorption and desorption to occur at the periphery of the nuclei" whereas our model specifically includes separate rate constants for those processes at the cluster surface. As far as the part of the interface not covered by clusters is concerned, we know of no reliable evidence for slow desad kinetics at the mercury-water interface other than those associated with the formation and dissolution of molecular aggregates, such as condensed films or micelles.

We note that the common models for nucleation and growth are unidirectional, in that they do not consider the reverse process of cluster dissolution. Neither do they consider the subtleties of two-dimensional growth and dissolution, in which both the one-dimensional periphery and the two-dimensional area of a cluster are in direct contact with its surroundings. At any rate, Dr. Armstrong's insistence that our model describe equilibrium behavior and, simultaneously, fit the (inherently unidirectional) classical nucleation theory, would clearly be impossible to satisfy.

On the atomically smooth, defect-free interface between two liquids, nucleation of a new phase is often a strongly hindered process, which requires a substantial supersaturation in order to proceed with measurable speed. In the coexistence region, no substantial supersaturation can build up, and nucleation is therefore immeasurably slow. This is why we need not consider nucleation in our analysis. There is ample precedent for this. To give an example, Gierst et al. [10] reported the rates of growth and dissolution of clusters, on either side of the equilibrium potential, without any interference from nucleation. Measurements such as shown in Fig. 6 of ref. 10 clearly imply the existence of a potential at which the net growth is zero. This is precisely the condition of coexistence.

We are not dealing here with a single potential, but with a narrow range of potentials, if only of a few millivolts, over which the rate of nucleation is negligible. (With isoquinoline [10], that range is much larger once the lumen of the capillary, the apparent locus of heterogeneous nucleation, is covered.) As long as the amplitude of our alternating voltage stays within this region, nucleation is slow enough to be ignored. Consequently there is no difficulty in envisioning a situation in which nucleation has effectively stopped while growth and its reverse, dissolution, are still active, because these latter processes do not require supersaturation. In fact, it is the very presence of a sufficient number of clusters that prevents any appreciable supersaturation.

Such behavior is, of course, different from that usually observed for electrodeposition on polycrystalline metals, to which Dr. Armstrong refers repeatedly. Polycrystalline surfaces typically contain many defects, which can act as nucleation sites; in their presence, nucleation will occur with little or no kinetic hindrance. For our studies at the usually defect-free mercury-water interface, a more pertinent faradaic analog is the deposition of silver on silver surfaces free of screw dislocations. In that case, there is again a range of overpotentials at which the rate of nucleation is immeasurably small [11]. A similar situation was observed with the mercury deposition on graphite [12].

Another aspect which has apparently confused Dr. Armstrong is that the aggregates we considered in [3] are not the critical nuclei, but much larger entities (specifically called clusters or patches to distinguish them from critical nuclei), large enough so that, together, they may cover a measurable fraction of the interface. This situation is somewhat analogous to that encountered with the so-called 'living polymers', which grow until the growth rate drops because the monomer concentration becomes too low [13]. However, the present, two-dimensional case differs in that it responds to the interfacial excess rather than the bulk monomer concentration, and that this interfacial excess is controlled by the applied potential.

Of course, coexistence of clusters and bare regions requires that the clusters were nucleated at some earlier time. In our admittance measurements, such nucleation most likely occurred during our initial efforts to locate the needle peak. We have already commented on the likelihood that, in the potential step experiments shown in Figures 5 and 6, nucleation resulted from overshoot during the initial stages of the step. Just to make sure, we measured the admittance in two ways: one by forming the drop at the potential of the needle peak, the other by forming it in the pit region, at -1.400 V, and by jumping to the potential of the needle peak after 10 s. These two methods yield the same admittance values within experimental error.

Dr. Armstrong chides us for the fact that our "model does not generate the discontinuity in electrode properties" that we do not observe. Since neither the Frumkin isotherm [14] nor the usual Ising model [15-17] addresses the kinetics of growth in the absence of nucleation, the relevance of his criticism in this respect eludes us.

Discontinuity

It is unfortunate that there appears to be a confusion in Dr. Armstrong's paper [5] between thermodynamics and kinetics. It has been demonstrated numerous times that the formation and dissolution of condensed films at the metal-solution interface is primarily a kinetic rather than a thermodynamic phenomenon. This point was made very explicitly in a recent review [18] under the telling title "The *dynamic* double layer". Arguments based on presumed thermodynamic properties, or on equilibrium models such as adsorption isotherms, may have only limited applicability. The fact that our experimental admittance data [3] show a resistive component clearly indicates that they are kinetic in nature. We are working under conditions such that the rate of nucleation is too small to affect our measurements, and at bulk concentrations such that mass transport is not a major rate-limiting factor. Under those conditions we can, in a number of cases, observe a **coexistence region** in which, judging by the interfacial capacitance, the fraction of the interface covered by the condensed film varies with applied potential in a reproducible and experimentally reversible manner [19,20]. Such behavior is often reflected by pit edges which are steep but not vertical. Dr. Armstrong posits that the experimental capacitance-potential curves exhibit a discontinuity at the phase transition, but the observations run counter to his opinion. This is a point that merits closer examination, and to which we intend to return in a separate communication, since the present, adversarial context is not really conducive to such a discussion.

The limitations of kinetic interpretations

Needle peaks have been reported for several other systems, among them camphor [21], 2,3-dimethylpyridine [22], thiourea [23] and guanidinium nitrate [9]. This suggests that we deal here with a rather general phenomenon. Moreover, we have observed that the admittance of the needle peak of 2,3-dimethylpyridine is quite similar to that of tetrabutyl ammonium bromide as reported in [3].

In kinetic studies we can exclude with certainty those models which clearly do not fit the experimental evidence. In our case this applies to a discontinuous capacitance change without a kinetic component, and to the Lorenz & Möckel desad model. On the other hand, we can never be completely sure that our interpretation is correct. In our earlier paper [3], we presented a plausible model for interpreting our experimental data, but the available experimental information was insufficient to assign specific numerical values to the various model parameters. The model led to an equivalent circuit that represents the key features of the data. On the other hand, that equivalent circuit is so simple that there are bound to be alternative models that can lead to a similar response. However, Dr. Armstrong has not offered any such alternative.

The perpetual motion machine

Finally, Dr. Armstrong finds it "difficult to see how a nucleus could have the properties required by de Levie and Wandlowski since it would (when $r = r'$) be continuously acquiring molecules by incorporation at its edge whilst losing molecules from its center direct[ly] to the solution at the same rate." Dr. Armstrong then goes on to state that this behavior would violate microscopic reversibility, and that such a cluster "would be a perpetual motion machine, forever pumping molecules in at its edge and out at its centre." We certainly are not the first to propose such a mechanism. A similar situation was described by Wegner [24] for the growth of actin polymers, where the growth rates at the two growing ends of the polymer are different. The resulting "head to tail polymerization" or "treadmilling" has been confirmed amply by different kinds of experiments and by a variety of workers, and has already been incorporated in the standard undergraduate curriculum in cell biology [25]. There is nothing thermodynamically or kinetically wrong with such a dynamic process. Brownian motion and exchange current densities could also be labeled "perpetual motion machines", but that does not bring them in conflict with any thermodynamic laws either. Not only are the two proposed processes taking place at different locations (which expose different 'sides' of the molecules forming the cluster, as in the case of the treadmilling polymers) but conceivably they may also involve different species: the reaction at the cluster periphery is with molecules adsorbed at the metal-solution interface, while those at the cluster-solution interface are not in contact with the metal, and consequently may well have a different solvent coordination.

Again, what is not possible with a sphere, where all interactions must occur through the same interface, is quite feasible at an interface, where a two-dimensional cluster shares both a periphery and an interface with its environment, or in one dimension, where two different ends of a polymer have different chemical properties. It appears that, once more, Dr. Armstrong may have been confused by analogs of a different dimensionality.

Conclusion

Dr. Armstrong states that there is a discontinuity in the capacitance-potential curve where, based on our experimental data and on those of others, this need not be the case. He opines that the data we reported must either depend on the amplitude of the applied sinusoidal signal, or fit a desad peak according to the model calculations of Melik-Gaikazyan & Frumkin and Lorenz & Möckel. Neither is correct. His accusation that our theory violates standard nucleation theory is irrelevant, since we work under conditions where nucleation does not occur. His invocation of the principle of microscopic reversibility is inappropriate. We therefore rest our case; the reader be the judge.

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Figure legends

Fig. 1. The interfacial capacitance Y_{el}/ω at the needle peak (at -1.54 V) measured with a Solartron 1250 frequency response analyzer at 7 points per decade between 0.1 Hz and 1 kHz. Amplitude of the sinusoidal signal used: (*) 1.0 mV, (+) 0.5 mV, and (▲) 0.25 mV. Data shown here in a complex capacitance plot are the average of five subsequent series of measurements, after correction for a solution resistance of 120 Ω, as determined by extrapolation to infinite frequency of the cell impedance, measured to 10 kHz. Hg in aqueous 0.5 M NaBr + 3 mM TBABr, temperature 5°C, frequencies marked at 0.1 , 1 and 10 Hz.

Fig. 2. Double-logarithmic representation of the absolute value of the measured electrode admittance $|Y_{el}|$, in S, as a function of frequency $f = 2\pi\omega$, in Hz, for the three amplitudes of the sinusoidal signal used: (*) 1.0 mV, (+) 0.5 mV, and (▲) 0.25 mV. Also shown on the same scale are measurements of the double frequency response, plotted in corresponding units of the magnitude $|i_{2\omega}|$ of the double-frequency current $i_{2\omega}$ divided by the amplitude ΔE of the sinusoidal signal used. Again, data are shown for the three amplitudes of the sinusoidal signal used: (*) 1.0 mV, (+) 0.5 mV, and (▲) 0.25 mV. All data pertain to Hg in aqueous 0.5 M NaBr + 3 mM TBABr, temperature 5°C.

Fig. 3. The interfacial capacitance of mercury in contact with aqueous 0.5 M NaBr + 3 mM tetrabutylammonium bromide at 5°C, scanned at -1 mV s^{-1}. Two curves are shown, at 20 Hz for 0.25 and 0.5 mV amplitude respectively, as indicated with the data. Moreover, discrete points show the capacitance 100 s after single potential steps to the various potentials, starting from -1.400 V (filled circles) and -1.700 V (open circles) respectively, measured at 20 Hz with 1 mV amplitude.

Fig. 4. Single potential step measurements starting at a potential E_1 = -1.400 V (inside the capacitance pit), at which value the mercury drop is kept for 10 s . The final potential E_2 is indicated with the curves, in V. As E_2 becomes more negative, the capacitance rises, goes through a maximum at the needle peak and, finally, decreases. Amplitude of the sinusoidal signal used: 1.0 mV; frequency 2 kHz. Each transient is measured on a fresh drop. Hg in aqueous 0.5 M NaBr + 3 mM TBABr, temperature 5°C.

Fig. 5. The same as in Fig. 4 but now starting at E_1 = -1.700 V, i.e., outside the pit, and stepping closer to and eventually into the pit region. Amplitude of the sinusidal signal used: 1.0 mV; frequency 2 kHz. Hg in aqueous 0.5 M NaBr + 3 mM TBABr, temperature 5°C.

Fig. 6. Double potential step experiments similar to those of Fig. 5, except that the potential sequence used was E_1 = -1.700 V for 10 s, E_2 = -1.526 V for τ_2 ms (as indicated with the curves), E_3 = -1.540 V. Curves shown starting with the transition $E_1 \rightarrow E_2$. Note that essentially the same capacitance is reached regardless of the dwell time at -1.526 V. Hg in aqueous 0.5 M NaBr + 3 mM TBABr, amplitude 1.0 mV, frequency 2 kHz, temp. 5°C.

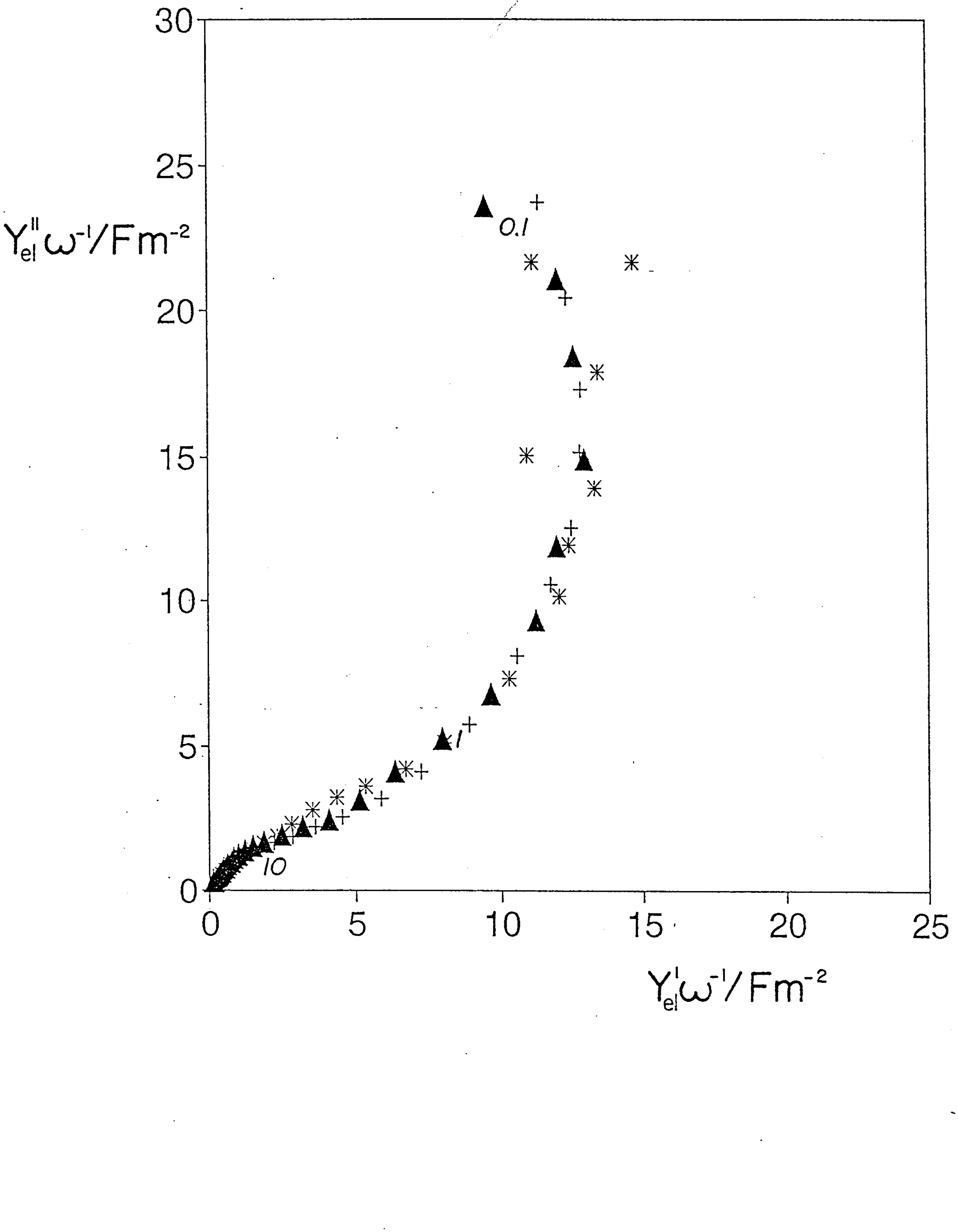
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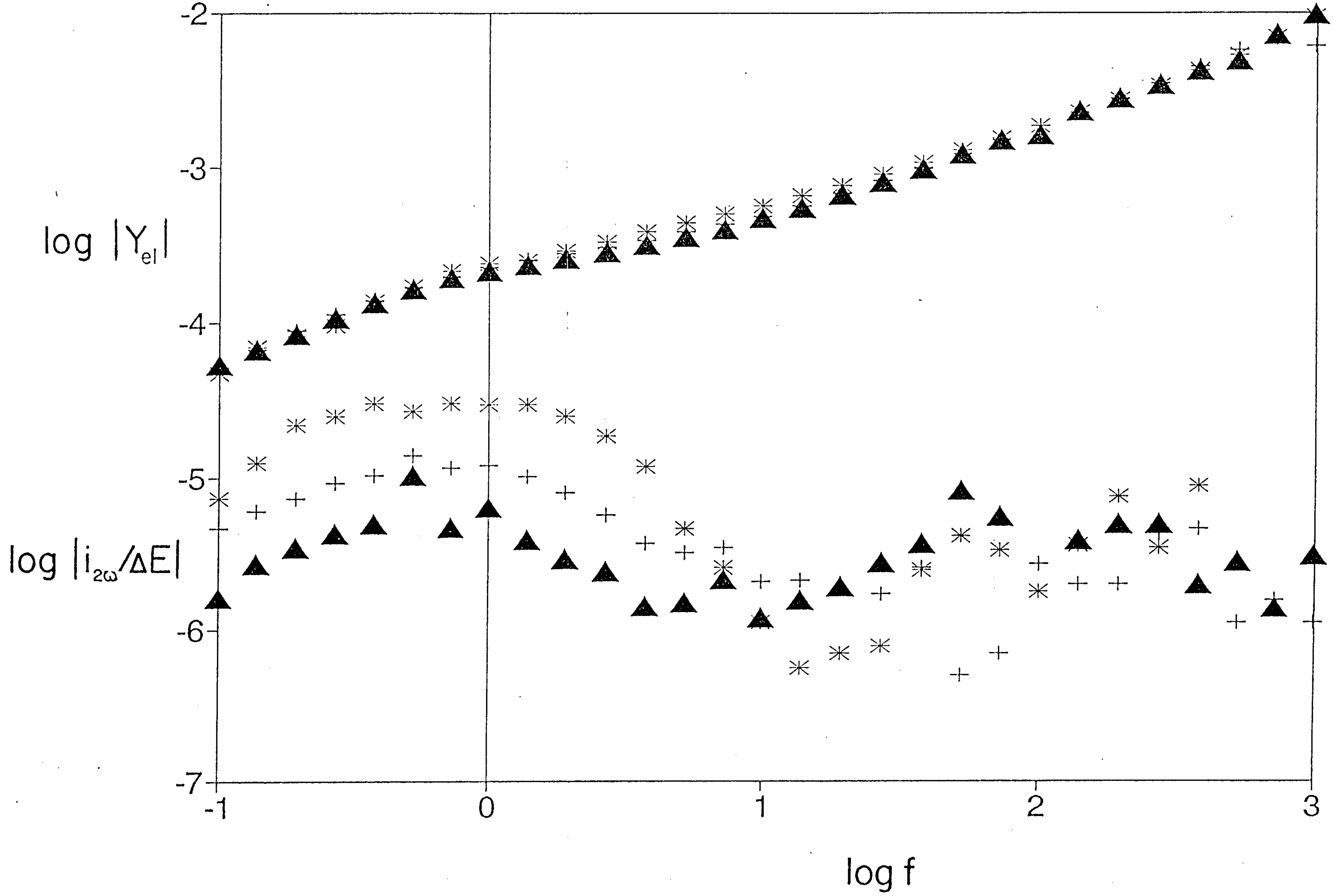
FIG. 1



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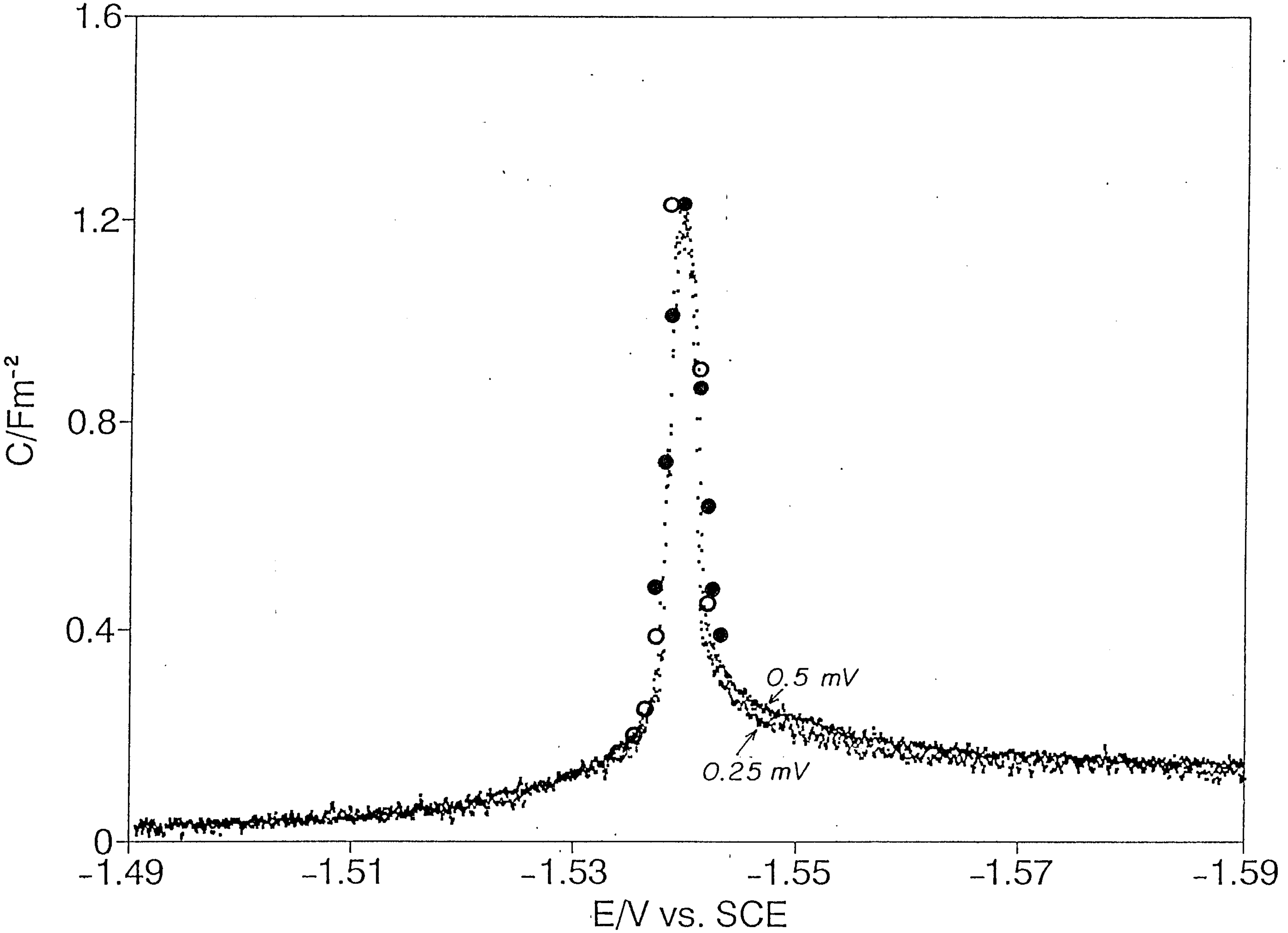

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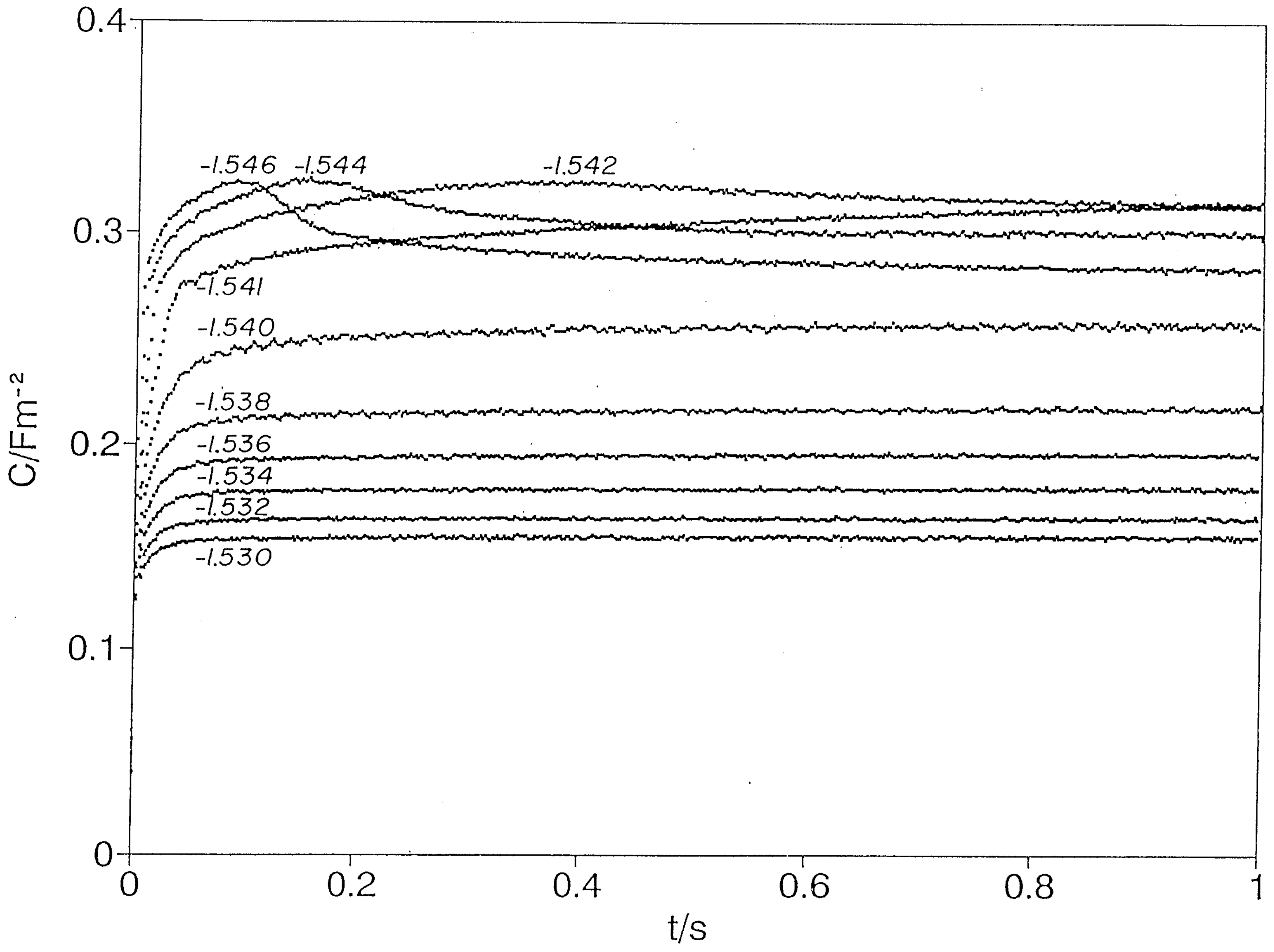
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FIG. 4

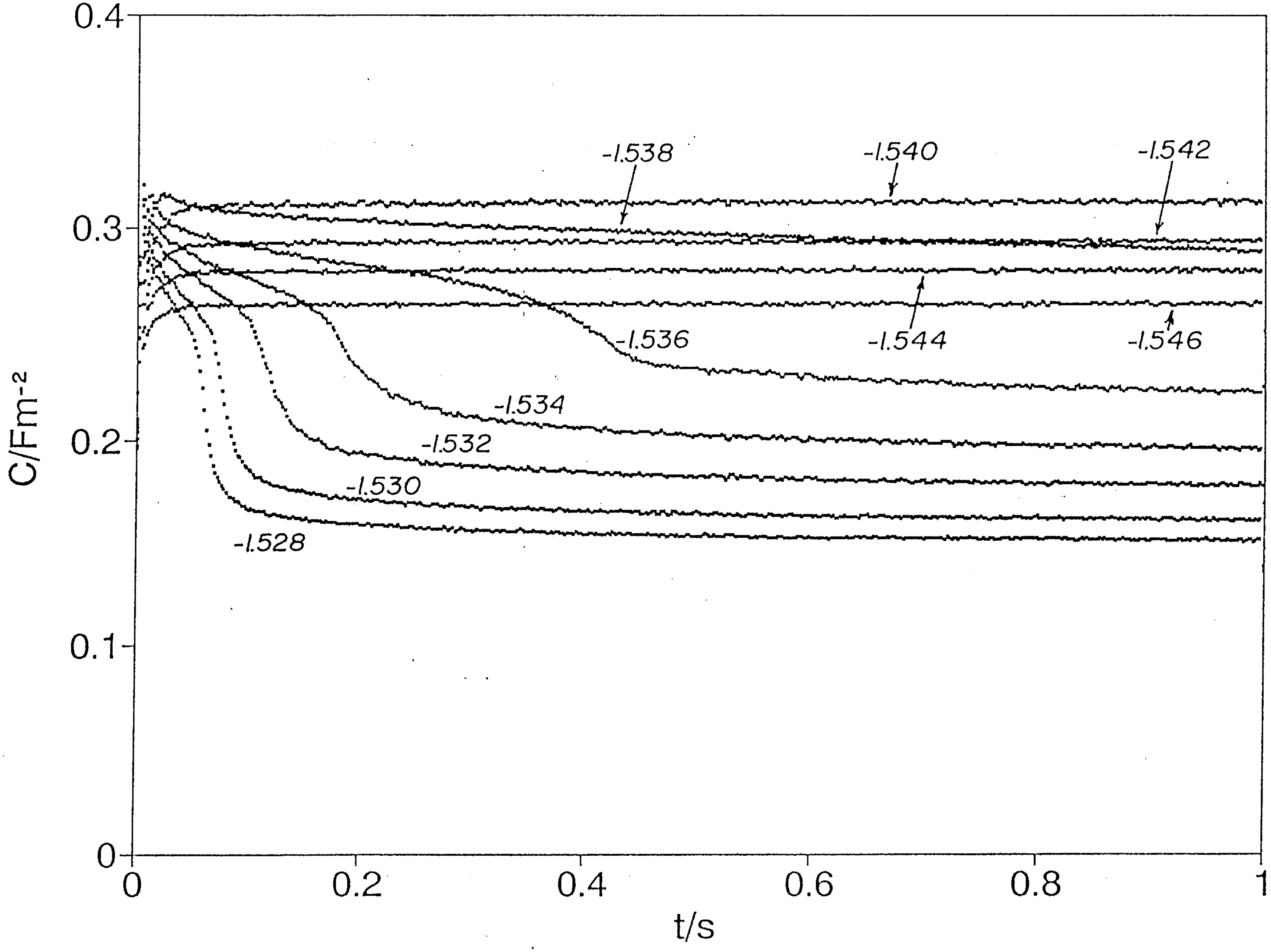
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FIG. 5

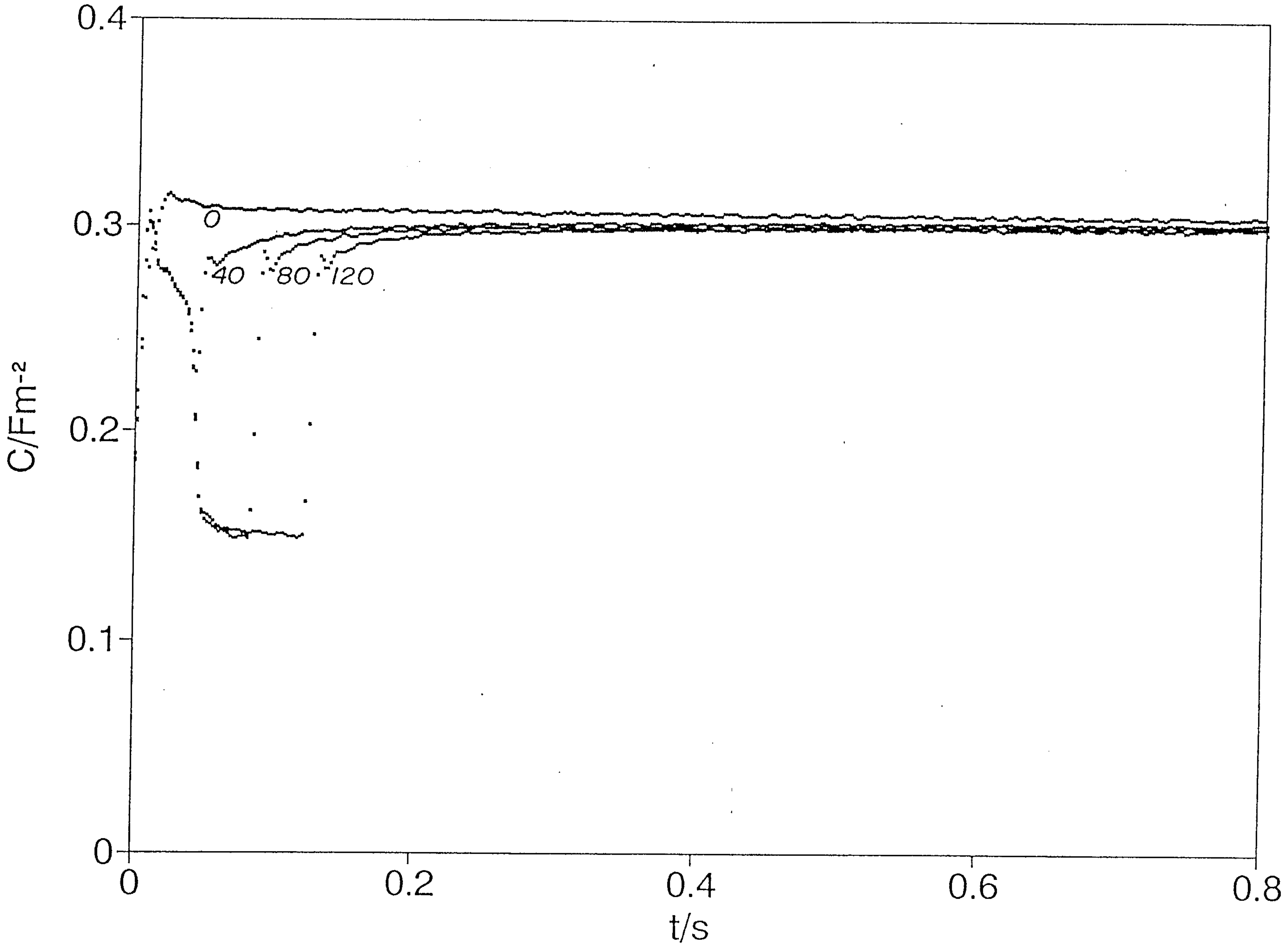

FIG. 6