Interference of Adsorption, Condensation, and Double-Layer Charging in Kinetic Studies of Film Formation. 2. Nonconstant Double-Layer Potential

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The single-potential-step technique is a useful electrochemical method for kinetic studies of phase transitions on electrodes. Under ideal conditions the final potential acts in the double layer immediately after the potental step is finished. But in experiments due to the finite time constants of the different electrode processes, the processes take place simultaneously and therefore influence each another. The measured current response contains the different parts of current, like double-layer charging due to the potential step, adsorption, and condensation more or less distinguishable according to the cell and kinetic parameters. For the experimental conditions this means that the entire electrode process, including the above-mentioned processes, takes place with a variable local double-layer potential. To describe such "nonpotentiostatic" conditions, the model of a coupled adsorption and nucleation and growth process (Part 1) is extended by a time dependent potential evolution, which again depends on the adsorption and condensation. Possible current transients were simulated with the help of the extended model and compared with the corresponding current transients in Part 1. Dependent on the cell resistance, the transients change their shape.

1. Introduction

In analyzing the potential dependent kinetics of adsorption of uncharged organic molecules, for example in the context of a two-dimensional phase transition in the adsorbed phase, it usually is assumed that after an applied potential step the adjustment of the final potential is much faster than all other processes under consideration. For such cases the applied potential step immediately begins to act at the double layer itself. In other words, the entire adsorption process of organic molecules itself can be considered as a potentiostatic process. Up to now, all models which were developed to interpret adsorption and two-dimensional phase transitions have taken only this potentiostatic case into consideration.[1−7]

This ideal potentiostatic condition is fulfilled if the time constants of the charging/discharging process due to the applied potential step and the adsorption process including the condensation can be clearly distinguished. On one hand, high supporting electrolyte concentrations and smooth electrode surfaces with small capacities lower the time constant RC. Additionally, a small difference ΔE between the starting and final potentials in the potential step experiments lowers the entire charge, which flows to reach the latter potential. But it should be mentioned that the starting potential must be at least located at a potential where the electrode surface can be considered as free from adsorbed organic molecules.

On the other hand, a clear distinction between the time constants of the interface processes can be achieved, if the adsorption kinetics is slow compared with the cell constant RC. This condition is often fulfilled on final potentials far away from the potential of maximum adsorption, where the adsorption coefficient reaches its maximum.

All these experimental conditions for truly potentiostatic measurements restrict the potential region, where the current response after an applied potential step can be unmistakably interpreted in the framework of the well-known adsorption as well as condensation models.[1−7]

But in many cases, the time constants for the adsorption and condensation processes as well as for the double-layer charging/discharging according to the potential step have the same order of magnitude. Even if the cell constant RC is low, the adsorption and condensation kinetics becomes very fast near the potential of maximum adsorption as well as on heterogeneous surfaces, where the activation energy is lowered by active sites.

For these cases the transition between the surface state at the starting potential, where the electrode surface is free from adsorbed molecules, and the surface state at the final potential, where the electrode surface is covered with a condensed phase of the adsorbed molecules, takes place under "nonpotentiostatic" conditions.

The different partial currents forming the total current response, which must flow during the transition, influence each other and can therefore not be considered to be independent. Any measurement of the entire adsorption kinetics would then be misinterpreted, if one considers an instantaneous change of the local potential at the double layer. Obviously, in this case also the local potential at the electrode surface will change gradually according to the capacitor charging/discharging time, respectively.

One possible model to describe a condensation of organic molecules via a nucleation and growth process is proposed in ref 12. A main feature of this model is the time dependent supersaturation as a consequence of the adsorption of

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organic molecules from the bulk onto the electrode and the consumption of such molecules due to growing condensed islands. In part 1[11] of this series of papers, this model was used to simulate current transients in condensation experiments with constant local double-layer potentials at the electrode surface.

The aim of the present paper is to develop a mathematical model on the basis of the model described above, which takes into account the interdependent processes of the double-layer charging of the pure electrode surface and the adsorption/condensation process. In the last consequence, this means that the proposed model describes the adsorption/condensation under conditions where the local potential at the double layer becomes time-dependent. As in part 1, the new "nonpotentiostatic" model is analyzed using numerical methods to solve the corresponding differential equations. The simulations of the current transients demonstrate the complex dependence of the current response on the experimental settings and the development of the different partial currents on these settings.

2. Theory

2.1. Extension of the Model of Coupled Adsorption and Condensation. In the previous paper (part 1) a model was developed describing the shape of the current transients occurring after a potential jump into the pit region from outside. In that model different processes responsible for the total current response could be separated: the changes in the double-layer charge due to adsorption and film formation kinetics and due to reorientation effects. The derivation of the model followed the common assumption that the final potential at the double layer can be reached instantaneously, which is a reasonable approximation if the time constant for the double-layer charging is much smaller than the time constant for the adsorption kinetics. However, as was pointed out above, there are also experimental situations where the potential change immediately at the double layer from the starting to the final potential occurs with a finite rate, which can be compared to the adsorption rate. Hence a more complete model has to take into consideration also the process of the increase (or decrease) of the potential immediately at the double layer and the coupling of even this potential evolution with the adsorption and condensation processes.

The expression for the time dependent total current density caused by the surface charging (or discharging) can be obtained, as shown in part 1, if one differentiates the mean charge density of an electrode surface which is partially covered by the condensed phase of the adsorbate,

$$q(t) = \Theta q_{film}(E) + (1 - \Theta)[q_0(E)(1 - \kappa\Gamma_a) + q_a(E)\kappa\Gamma_a] \tag{1}$$

against time. Here $\kappa = \Gamma_{film}/\Gamma_{max}$. For simplicity, in the following it will be assumed, as in part 1, that $\kappa = 1$, that is, $\Gamma_{max} = \Gamma_{film}$. This is valid if the occupation area of adsorbed molecules does not significantly change during the condensation process. However, if significant reorientation takes place and $\kappa > 1$, the shapes of the later

simulated current–time transients will not change qualitatively, as can be seen from eq 3. Obviously, if a given experimental system should be simulated from which it is known that a reorientation and a remarkable change in the area occupied by an adsorbed molecule take place, the equations with a $\kappa \neq 1$ should be used.

The mean charge density is composed of the partial charges per unit surface of the adsorbate free surface $q_0(E)$, of the complete monolayer without reorientation $q_a(E)$, and of the condensed adsorbate monolayer considering reorientation effects $q_{film}(E)$. Γ_a is the surface concentration of the adsorbed expanded phase, measured in units of the density of the condensed film Γ_{film}. Γ_{max} is the maximum possible surface concentration of the adsorbed expanded phase (for the formal limit of infinite bulk concentration). Θ is the ratio of the area of the film-covered surface to the entire surface area. To be compatible with the dimensionless variables used in part 1 (time, length, surface concentration), also the electrical variables (potential, absolute charge, and absolute capacity) can be nondimensionalized formally by dividing by some convenient SI units: $U_{unit} = 1$ V, $Q_{unit} = 1$ μC, $C_{unit} = 1$ μF.

To obtain the expression for the complete capacitive current, one has to differentiate also the double-layer potential E itself, which is no longer a constant as in part 1:

$$i(t) = \{q_{film}(E) - [q_0(E)(1 - \kappa\Gamma_a) + q_a(E)\kappa\Gamma_a]\}\frac{d\Theta}{dt} +$$
$$(1 - \Theta)[q_a(E) - q_0(E)]\kappa\frac{d\Gamma_a}{dt} + \left\{\Theta\frac{dq_{film}(E)}{dE} +\right.$$
$$\left.(1 - \Theta)\left[\frac{dq_0(E)}{dE}(1 - \kappa\Gamma_a) + \frac{dq_a(E)}{dE}\kappa\Gamma_a\right]\right\}\frac{dE}{dt} \tag{2}$$

Again, the first two terms in eq 2 can be transformed to a more transparent form, identifying the partial currents responsible for the adsorptive source process and for the reorientation process during the film formation, respectively:

$$i(t) = (1 - \Theta)(q_a - q_0)\kappa\left[\frac{d\Gamma_a}{dt}\right]_+ - [(q_a - q_{film}) +$$
$$(\kappa - 1)(q_a - q_0)\Gamma_a]\frac{d\Theta}{dt} + \bar{C}(E,\Theta,\Gamma_a)\frac{dE}{dt} \tag{3}$$

with

$$\left[\frac{d\Gamma_a}{dt}\right]_+ = \alpha(\gamma - \Gamma_a) \tag{4}$$

and

$$\bar{C}(E,\Theta,\Gamma_a) = \Theta C_{film}(E) + (1 - \Theta)[C_0(E)(1 - \kappa\Gamma_a) + C_a(E)\kappa\Gamma_a] \tag{5}$$

Here α is the nondimensionalized form of the effective adsorption rate constant, whereas γ is the dimensionless equilibrium concentration of the adsorbate (for the mathematical definition, see part 1).

The third term in eq 3 is the additional partial current caused by the establishment of the final potential at the double layer. Equation 5 is some mean capacity (per unit surface), which represents the weighted sum of the partial capacities $C_0(E)$, $C_a(E)$, and $C_{film}(E)$. This mean capacity should not be confused with the mean differential capacity, which additionally contains the derivatives of the coverages.

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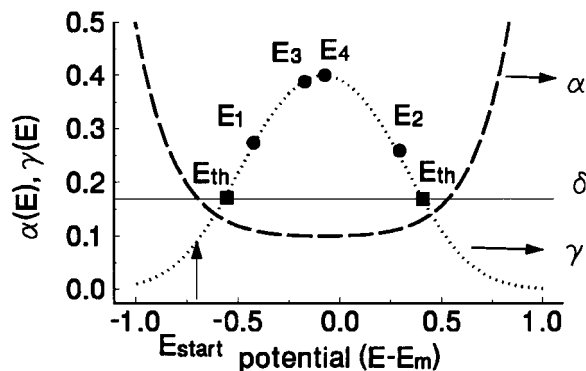
Figure 1. $\gamma(E)$ and $\alpha(E)$ versus potential, respectively: γ-$(E)-E$, $\cdots$; $\alpha(E)-E$, $---$. E_{start} represents the starting potential for all presented simulations, E_x represent the final potentials according to the different possible positions of these potentials with respect to the charge potential curves, E_{th} represents the thermodynamic transition potential.

To complete the system of differential equations capable of describing the entire process of adsorption, double-layer charging, and condensation, one has to add another differential equation for the double-layer potential to the equations of the adsorption and film formation (eqs 1−4 in part 1). This equation can be obtained from the description of the electrical circuit, in which the (variable) capacity of the double layer is in series with the ohmic resistance R of the electrolyte solution and the voltage source of the potentiostat U:

$$S_0 i(t) = \frac{U - E(t)}{R} \tag{6}$$

Here, S_0 is the area of the working electrode and E is the actual double-layer potential. i is the current density. To fulfill the dimensional relations, the resistance here has the dimension $R_{unit} = (U_{unit}/Q_{unit})t_{unit}$, where the time unit was defined in part 1.

The insertion of eq 3 for the current density $i(t)$ and rearrangement then leads to the equation for the double-layer potential $E(t)$:

$$\bar{C}(E,\Theta,\Gamma_a)\frac{dE}{dt} = \frac{U - E}{RS_0} - (1 - \Theta)[q_a(E) -$$

$$q_0(E)]\kappa\left[\frac{d\Gamma_a}{dt}\right]_+ + [(q_0(E) - q_{film}(E)) +$$

$$(\kappa - 1)(q_a(E) - q_0(E))\Gamma_a]\frac{d\Theta}{dt} \tag{7}$$

Now eq 7 together with eqs 1−4 from part 1, describing the adsorption and condensation kinetics, form a closed system of differential equations for the general problem of a time dependent double-layer potential. This system can be solved numerically to simulate all possible current transients.

2.2. Numerical Simulations. The change in the shape of current transients depending on the position of the final potential in comparison with that of the potential of maximum adsorption E_m is described in detail in part 1 for the potentiostatic case.

Figure 1 shows the potential dependence of the dimensionless parameters α and γ. The course of these two curves is assumed to be the same for all simulations carried out. It is also assumed that the potential dependence of α and γ is symmetrical to the origin at $E = E_m$. The minimum value of α is 0.1, and the maximum value of γ is 0.4. The parameter set for α and γ was borrowed from ref 12. It

should be mentionend once again that, contrary to the simulations for the potentiostatic case, where the parameters α and γ are constant during the phase transition, in the present case the actual values of the parameters α and γ move on the $\alpha(E)$ and $\gamma(E)$ potential curves from the starting potential to the final potentials, depending on the potential evolution during the entire phase transition process (Figure 1).

The intersection point between the γ curve and the dimensionless saturation concentration line δ represents the thermodynamic transition potential. Figure 1 shows the starting potential, which lies always outside the condensation region at the potential −0.7, and the corresponding final potentials for the simulations. The potentials E_3 and E_4 are only relevant for the discussion of transients obtained in systems where reorientation occurs. In these systems three characteristic intersection points E_m, E'_m, and E_{cp} occur instead of the one point E_m in systems where no reorientation occurs. E_{cp} is the potential where the charge potential curves for the equilibrium concentration of the noncondensed phase and the condensed phase intersect. E'_m is the potential where the charge potential curves for the free surface concentration and the condensed phase intersect. E_m is the potential where the charge potential curve for the equilibrium concentration of the noncondensed phase and the charge potential curve for the free surface concentration intersect. In agreement with part 1, the parameters $\delta = 0.166$, $\kappa = 1$, and $K = 0.076$ have the same values for all presented simulations.

The capacity of the adsorbate-free electrode is fixed at $C_0 = 1.94$, and the capacity of the complete-adsorbate-covered surface is fixed at $C_a = 0.86$. The capacity values are based on the slopes of typical experimentally obtained charge−potential curves.[8] For the sake of simplicity, the capacities of the condensed monolayer and the complete noncondensed monolayer are assumed to be equal. The potential of zero charge PZC is 0 V. The shift in the PZC, E_n, for a complete condensed monolayer without reorientation is fixed at 0.1 V, whereas, in systems where reorientation occurs, the shift E'_n is fixed at 0.2 V. These potential and capacity data determine the charge−potential curves as well as the intersection points E_m, E'_m, and E_{cp}.

To demonstrate the changes in the shapes of current transients according to a transition from conditions with time-independent double-layer potentials (absolute potentiostatic conditions) to conditions with time dependent double-layer potentials ("nonpotentiostatic" conditions), in the following simulations the solution resistance is varied to influence the cell constant RC.

Final Potential E_1. If the potential step takes place from the starting potential to the final potential E_1, then the sign of the double-layer charging due to the potential step equals the sign of the adsorption and condensation current (see Figure 3 a).

In the figure, series 2 simulated current transients for such a potential step are shown. In Figure 2a and c the transients were obtained, without reorientation occurring during the phase transition, whereas in Figure 2b and d the molecules undergo reorientation in the system. For all these conditions the total current response has formally the well-known nonmonotonic current shape, which is characteristic for nucleation and growth processes in adsorbate systems.

Figure 2a and b represents simulations for a low solution resistance ($R = 1$). The double-layer charging of the adsorbate-free electrode surface is mostly finished when the condensation begins. Merely at the very beginning of
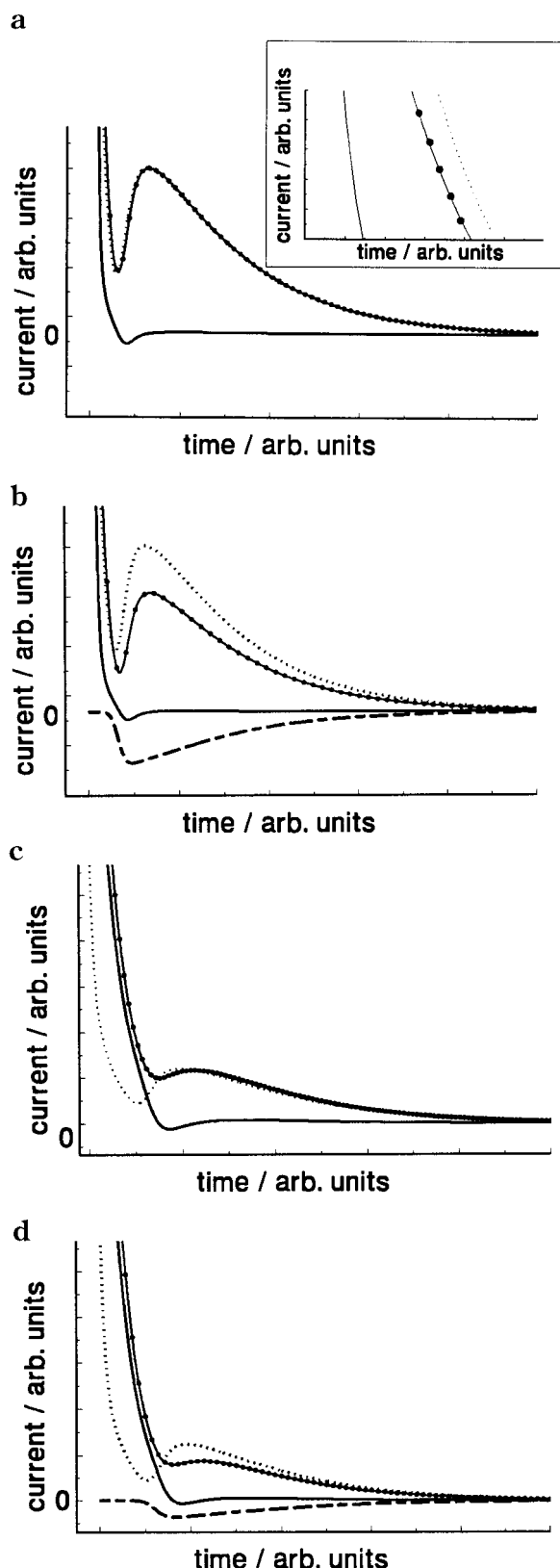
a

b

c

d

Figure 2. Simulated current−time transients for a potential step $E_{start} - E_1$. Parts a and b represent a low-resistance cell ($R = 1$): (a) without reorientation during the phase transition; (b) with reorientation during the phase transition. Parts c and d represent a high-resistance cell ($R = 20$): (c) without reorientation during the phase transition; (d) with reorientation during the phase transition. (···) pure adsorption current; (− - −) reorientation current; (−) double-layer charging current; (− with full circles) total current response; (inset) zoom of the above-presented current transients at the very beginning of the process.
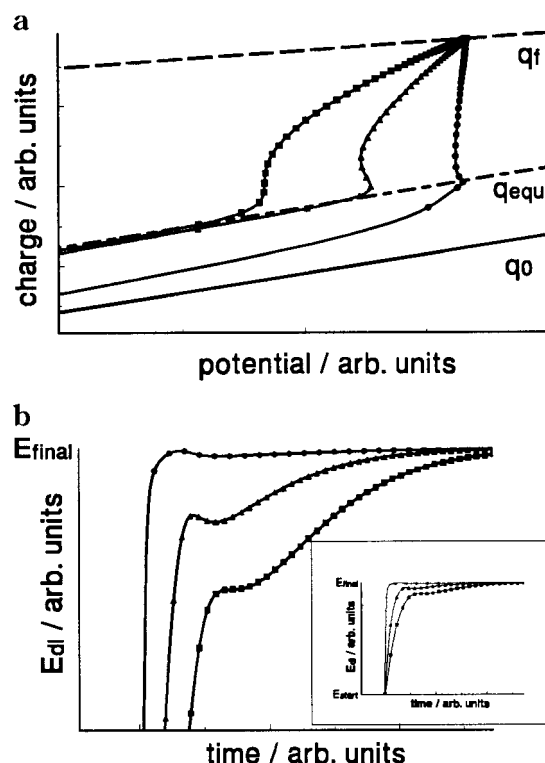
a

b

Figure 3. (a) charge−potential curves corresponding to the current−time transients in Figure 2b and d. (b) Double-layer potential−time curves corresponding to the current−time transients in Figure 2b and d. Cell resistances: $R = 1$ (solid circle); $R = 10$ (triangle up solid); $R = 20$ (solid box). q_0, charge−potential curve of the adsorbate-free surface; q_{equ}, charge−potential curve for the equilibrium concentration of noncondensed molecules; q_{film}, charge−potential curve for the condensed-film-covered surface.

the charging process immediately after the potential step has occurred, the double-layer charging of the pure electrode surface and the adsorption process take place simultaneously. These interdependent processes cause a shift in the total current response in comparison with the pure adsorption current on the time axis to higher times (for example, see the inset in Figure 2a). Exactly as for the potentiostatic case in part 1, the total current response differs from the real adsorption current in reorientation systems by the additional dipole contribution (Figure 2b).

Parts a and b of Figure 3 present the corresponding charge−potential and potential−time curves, respectively. It is obvious from this, that the transition from an adsorbate-free surface to an adsorbate-covered surface before the nucleation begins takes place under nonpotentiostatic conditions, whereas the condensation itself occurs under nearly potentiostatic conditions. Furthermore, it is interesting to note that the pure double-layer charging of the adsorbate free-surface is not a simple exponential decaying current. For both reorientation and no reorientation cases, this partial current passes a minimum when the condensation begins. As a result, the potential−time evolution is also not a simple exponential function (Figure 3b). At the beginning of the condensation, the final potential is already reached. But then, after nucleation has started, the potential is once again slightly lowered and curved again to the final potential (Figure 3a). How can this s-shape in the charge−potential curve be explained?

The condensation process suddenly lowers the dielectric constant of the surface condensor due to the formation of the more dense condensed phase. Therefore, the transition

between the condensor C_a (noncondensed phase) and the condensor C_{film} (condensed phase) causes a discharging current. If this current has a finite time constant due to the cell resistance, this would mean that the surface charge cannot drain fast enough and that an excess charge is temporarily located at the surface. Consequently, as long as the charge is not balanced, the local double-layer potential decreases. This effect becomes stronger with increasing cell resistance, as is demonstrated in the next example and in Figure 3a.

How does the shape of the current response change when the solution resistance is comparably high ($R = 20$)? Figure 2c and d shows examples for current–time transients in no reorientation/reorientation cases.

The condensation begins when the pure double-layer charging is not finished. This means that almost the entire adsorption and condensation process takes place under conditions where the final potential is not reached (Figure 3a). Compared with the real adsorption current, on one hand, the total current response is shifted on the time axis and, on the other hand, the minimum and maximum become less pronounced by the double-layer contribution. By no means does the total current response represent the adsorption kinetics as well as the condensation kinetics. As in the low-resistance case, the real condensation process causes at the very beginning an s-shape course of the charge–potential curve due to the delay of the excess charge flows during the condensation process. As mentioned above, the delay becomes more pronounced with increasing cell resistance.

Final Potential E_2. If one jumps from -0.7 V to the final potential E_2, then the sign of the discharging of the condensor C_0, representing the pure adsorbate-free surface, is positive, whereas the adsorption and condensation current at the final potential causes a negative charge flow (see Figure 5).

In Figure 4 examples for current transients in no reorientation/reorientation systems at low and high solution resistances are displayed. The analysis of the low-resistance transients leads to the following conclusions:

The additional contribution of charge due to reorientation leads to a more pronounced maximum in the total current compared with that for the pure adsorption current (compare parts a and b of Figure 4).

Although the cell resistance is low, it is sufficient to influence the adsorption at the very beginning of the process in such a way that the adsorption takes place under nonpotentiostatic conditions. Physically that means that both the final potential adjustment and the adsorption up to near equilibrium concentration take place simultaneously (see Figure 5a). As long as the actual potential is located negative of the potential E_m, the adsorption current must be positive. After passing this potential E_m, the sign of the adsorption current is turned to the opposite. Therefore, in Figure 4a and b the adsorption current and the total current response pass the zero line at the very beginning of the process and two minima appear in their shapes. The condensation process itself takes place at a constant double-layer potential, as is shown in Figure 5. The double-layer charging current responsible for the adjustment of the final potential forms a single oscillation with a minimum/maximum shape and is, like that for the final potential E_1, not a simple exponentially decaying contribution (see Figure 4a and b). In the charge–potential curve as well as in the potential–time curve this effect is reflected by exceeding the final potential E_2 in the positive direction with two maxima. Both excesses are caused by the lowering of the dielectric constant due to the adsorption
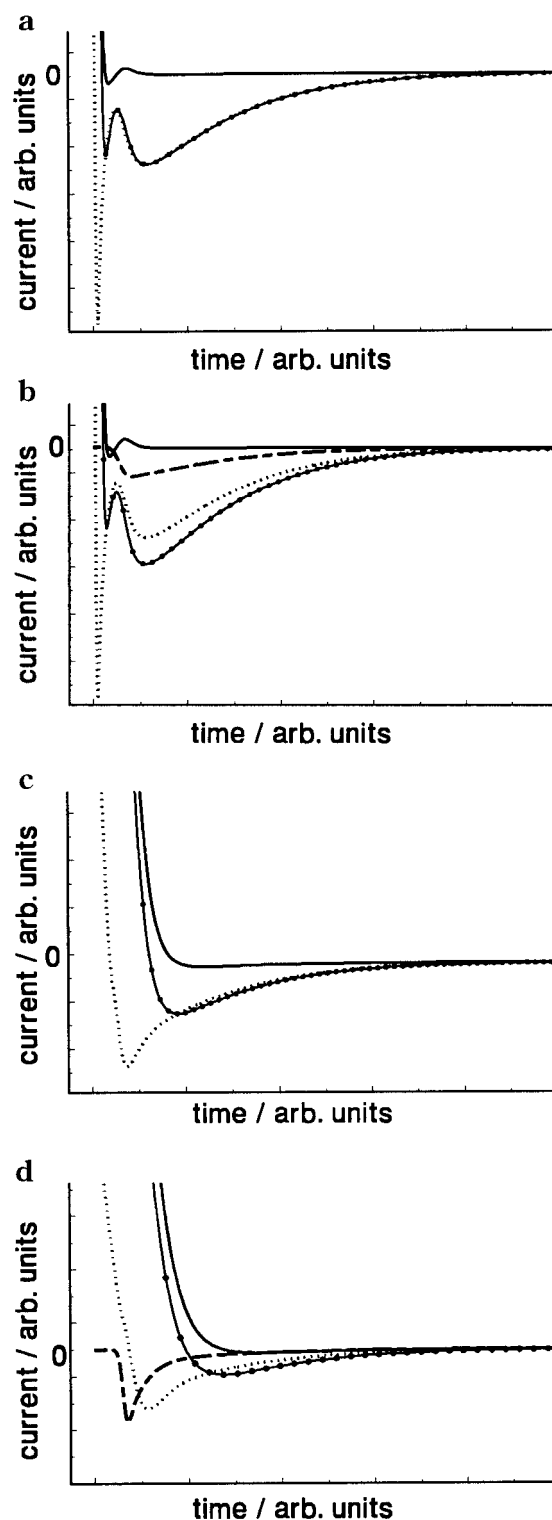

Figure 4. Simulated current–time transients for a potential step $E_{start} - E_2$. Parts a and b represent a low-resistance cell ($R = 1$): (a) without reorientation during the phase transition; (b) with reorientation during the phase transition. Parts c and d represent a high-resistance cell ($R = 20$): (c) without reorientation during the phase transition; (d) with reorientation during the phase transition. ($\cdots$) pure adsorption current; ($- \cdot -$) reorientation current; ($-$) double-layer charging current; ($-$ with full circles) total current response.

and condensation on one hand and the resulting delay in the necessary discharging due to the cell resistance on the other hand. Therefore, the reason for the nonmonotoneous charge–potential curve as well as for the potential–time curve is the same as that for the final potential
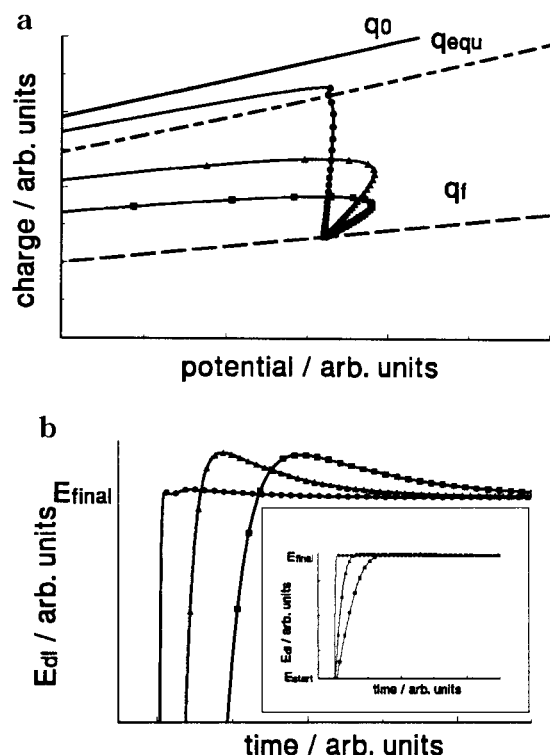
a

b

Figure 5. (a) charge−potential curves corresponding to the current−time transients in Figure 4b and d. (b) Double-layer potential−time curves corresponding to the current−time transients in Figure 4b and d. Cell resistances: $R = 1$ (solid circle); $R = 10$ (triangle up solid); $R = 20$ (solid box). q_0, charge−potential curve of the adsorbate-free surface; q_{equ}, charge−potential curve for the equilibrium concentration of noncondensed molecules; q_{film}, charge−potential curve for the condensed-film-covered surface.

E_1. But in the latter case, E_2, the potential is increased, whereas in the former case, E_1 the potential is decreased by the charge excess. Generally, for this low cell resistance the effect is very small and probably without any importance for the current response.

If the solution resistance is increased, then the total current response as well as the adsorption current exhibits only one minimum. As both the adsorption process and the condensation take place under conditions where the final potential adjustment is not finished, the critical nucleation concentration is nearly reached, before the potential E_m is passed. Therefore, the main part of the adsorption current is positive before condensation starts. The small negative charge contribution after passing E_m is vanishingly small in comparison to the positive double-layer charging current. When the condensation starts, the negative charge contribution due to the condensation itself and additionally due to the reorientation becomes greater than the double-layer charging current. Just now the current response becomes inverted.

Comparing the reorientation current in Figure 4d as an indicator for the real condensation process and the charging current responsible for the adjustment of the final potential, one can see that a main part of the surface is already covered with the condensed phase before the final potential is reached. For the high-resistance cell it also holds that the fast condensation temporarily causes a surface charge excess and, therefore, the actual potential moves to a more positive direction beyond the final potential (see also Figure 5a) until the charge excess vanishes. This effect becomes stronger with increasing solution resistance.

The considerations described above are valid independent of whether and in which direction reorientation takes place during the phase transition. Only the leveling or strengthening effect due to the additional reorientation current can be obtained.

From comparing the current transients obtained in the present simulations with the corresponding current transients in the pure potentiostatic case, part 1, it can be concluded that for a final potential E_1 the general shape of a current response, namely the nonmonotonous minimum/maximum shape, does not change qualitatively with the variation of the cell resistance. Therefore, it is very difficult to distinguish experimentally between a case with a constant and a case with a variable double-layer potential in experiments. The difference between the adsorption current and the total current response becomes greater with increasing solution resistance.

The transients obtained at the final potential E_2 can be clearly distinguished according to the conditions for the double-layer potential. Whereas in potentiostatic experiments the pure adsorption current and with it the total current response are always negative, in "nonpotentiostatic" experiments the adsorption current and the total current response change their sign according to the potential time evolution.

In systems where reorientation occurs, two additional potential regions, namely the first one between E_{cp} and E'_m and the second one between E'_m and E_m, can be separated, as described in detail in ref 8. For these potentials both the double-layer current, for the adsorbate-free surface and, at least, for the adjustment of the final potential, and the adsorption current are positive, whereas the sign of the reorientation current is negative. The difference in the current behavior between the final potentials E_3 and E_4 consists of the ratios of the charges for the adsorbate-free surface q_0, for the surface covered with the equilibrium concentration of the noncondensed phase q_{equ}, and for the surface covered with the condensed phase q_{film} at the final potential, respectively.

Final Potential E_3. For the final potential E_3 the following relationship is valid:

$$q_0 < q_{film} < q_{equ}$$

If the solution resistance is low, one obtains formally the same shape of current transients as was obtained for the case where the double-layer potential is constant (part 1), namely the single oscillation current response. This unusual shape is the result of the positive adsorption current and the negative reorientation contribution, as demonstrated in Figure 7a. The appearance of such a shape of current transients is the best proof for the interplay between the adsorption from the bulk and the condensation at the surface and the resulting time dependent surface concentration. Nevertheless, as is seen at the double-layer current in Figure 7a as well as in the charge−potential and the potential−time diagrams (Figure 8), a main part of the adsorption and condensation process takes place under conditions where the final potential is not reached. The charge−potential diagram (Figure 8a) is of interest: First, one obtains the excess of the potential already known from the final potential E_2. But then the charge−potential curve describes a loop back to the final potential. That means that the surface charge temporarily decreases. The last period of the condensation process takes place at a constant double-layer potential. The excess of the final potential is clearly caused by the already well-known lowering of the dielectric constant. But contrary to the case for the final potential E_2, where both the
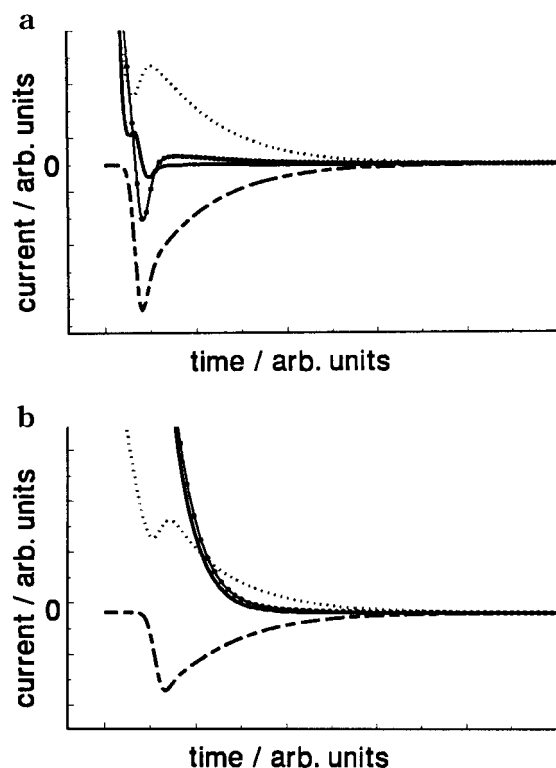
Figure 6. Simulated current- time transients for a potential step $E_{start} - E_3$. (a) Low-resistance cell ($R = 1$) with reorientation during the phase transition. (b) High-resistance cell ($R = 20$) with reorientation during the phase transition. ($\cdots$) pure adsorption current; ($- \cdot -$) reorientation current; ($-$) double-layer charging current; ($-$ with full circles) total current response.

adsorption and the condensation process cause a similar potential excess, in the present case the potential is raised solely due to the condensation process. This becomes clear if one considers the charge–potential curves (q_0, q_a, q_{film} vs E) in Figure 8a. Whereas the adsorption current is positive and therefore a charge-balance delay would cause a potential decline, the condensation/reorientation current is negative and therefore a corresponding charge-balance delay causes a potential rise. On the other hand, the suddenly starting condensation leads to a depletion of noncondensed molecules that lead to a decrease of the density of the expanded adsorbed phase, which is the reason for the loop in Figure 8a.

Why does no depletion of noncondensed molecules and the resulting charge potential loop occur in other potential regions? A possible reason can be—additionally to the opposite signs of the adsorption and reorientation current— that the absolute value of the charge which flows during the true condensation process is very small compared with other potentials ($(q_{film} - q_{equ}) \ll (q_0 - q_{film})$). On the other hand, such small effects such as the depletion of non-condensed molecules cause also absolutely only a very small change of charge. Therefore, these two currents are of comparable magnitude and can be distinguished in the simulation. At other potentials the small depletion effect on charges vanishes, seemingly due to the higher absolute value of the charge which flows during the condensation process.

If the solution resistance is comparably high ($R = 20$), the total current response behaves like a simple expo-nentially decaying current and follows the double-layer current responsible for the adjustment of the final potential (Figure 6b). The entire phase transition process takes place under "nonpotentiostatic" conditions, as is shown in Figure
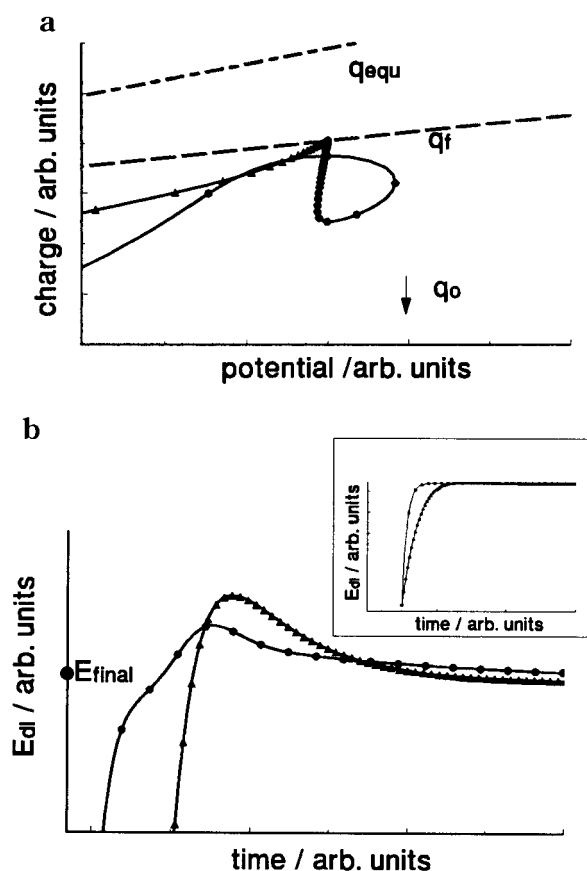

Figure 7. (a) Charge–potential curves corresponding to the current–time transients in Figure 6. (b) Double-layer potential–time curves corresponding to the current–time transients in Figure 6. Cell resistances: $R = 1$ (solid circle); $R = 20$ (triangle up solid) q_0, charge–potential curve of the adsorbate-free surface; q_{equ}, charge–potential curve for the equilibrium concentration of noncondensed molecules; q_{film}, charge–potential curve for the condensed-film-covered surface.

7. Nevertheless, the true adsorption current exhibits the already known minimum/maximum shape. But both the adsorption and the reorientation current cannot signifi-cantly influence the appearing shape of the current response.

Final Potential E_4. At the final potential E_4 the current response exhibits only one minimum and looks therefore like the "normal" inverted current transients[8] (Figure 8). This "inverted" shape appears independently from the solution resistance after passing the special potential E'_m. The minimum is more pronounced with decreasing solution resistance. Whereas all simulated transients at the final potential E_4 are similar in their appearing shape to the simulated transients at E_2 for a high resistance, the main difference in the current shapes between these two potentials appears clearly for low-resistance systems. At E_2 both the adsorption current and the reorientation current are negative, leading to two current minima in the total response signal under these conditions. Mean-while, at the potential E_4 only the reorientation contribu-tion is negative and the adsorption current is furthermore positive. Therefore, only one minimum can appear in a more or less pronounced way, depending on the cell resistance. In the first part of the entire adsorption process the total current response is determined by the positive double-layer charging and, additionally, by the adsorption current, whereas in the last part of condensation the current response is determined mainly by the reorientation current. The charge–potential curves as well as the
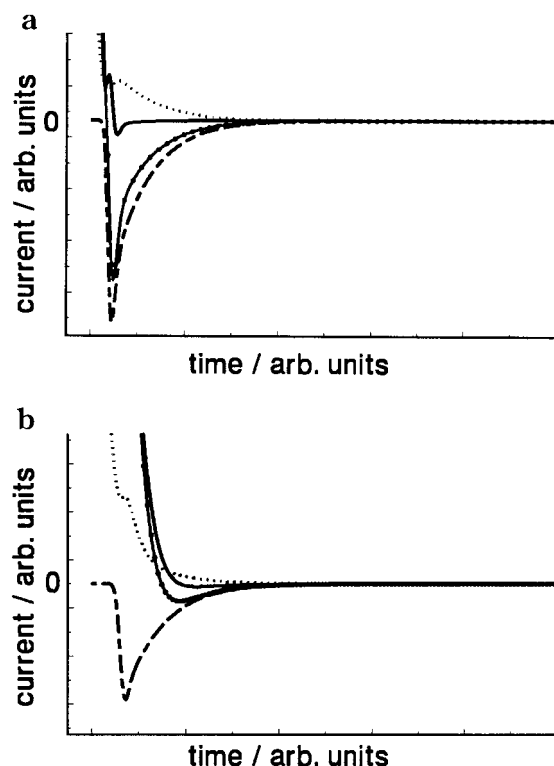
a

b

Figure 8. Simulated current−time transients for a potential step $E_{start} - E_4$. (a) Low-resistance cell ($R = 1$) with reorientation during the phase transition. (b) High-resistance cell ($R = 20$) with reorientation during the phase transition. (···) pure adsorption current; (− - −) reorientation current; (−) double-layer charging current; (− with full circles) total current response.

a

b

Figure 9. (a) Charge−potential curves corresponding to the current−time transients in Figure 8. (b) Double-layer potential−time curves corresponding to the current−time transients in Figure 8. Cell resistances: $R = 1$ (solid circle); $R = 20$ (triangle up solid). q_0, charge−potential curve of the adsorbate-free surface; q_{equ}, charge−potential curve for the equilibrium concentration of noncondensed molecules; q_{film}, charge−potential curve for the condensed-film-covered surface.

potential−time evolution (Figure 9) demonstrate the transition from a quasi potentiostatic to a "nonpotentiostatic" condensation process.

At this point it should be mentioned that the minimum in the total current response is further shifted on the time axis to higher times (compared with the minimum in the reorientation current) on increasing the solution resistance. At this potential it is very difficult to distinguish between the mostly potentiostatic condensation (Figure 8a) and the condensation with a variable double-layer potential (Figure 8b) solely from the shape of the total current response.

3. Summary

The simulations described above generate a wide variety of possible current transients in nonfaradaic two-dimensional phase-transition systems. Most of them (Figures 2, 4c and d, and 8) were already experimentally found, whereby the shape type presented in Figure 2 is the most investigated and modeled one. The simple inverted current transients (Figures 4c, and d and 8) were experimentally found and described in ref 8. Until now the unusual shape shown in Figure 6a was measured only as a single event (see part 1). The double-minima transients are not found experimentally up to now. The well-aimed investigation of such transients and the influence of the resistance on the current response signal at this potential are the subject of further investigations.

What can be concluded from the simulations described above?

If the potential step technique is applied for kinetic studies, in the current response always appears a double-layer charging/discharging part, which influences the
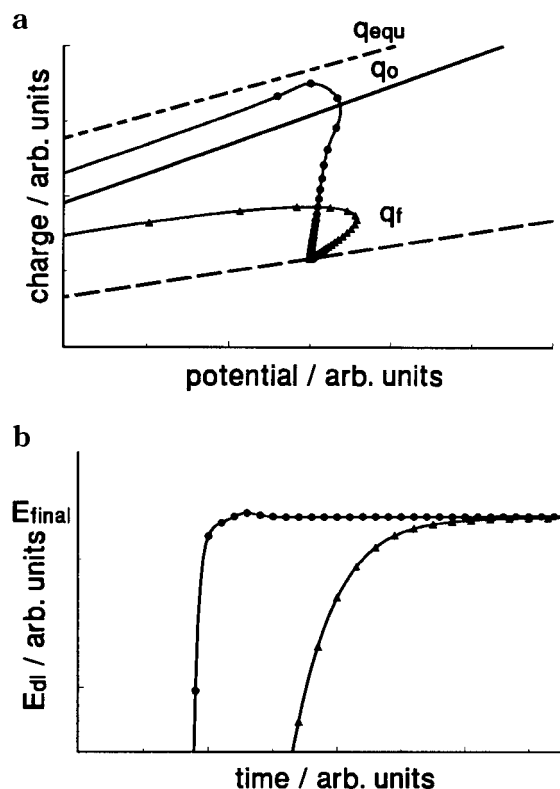
adsorption signal according to the solution resistance. In chronocoulometric studies this part must be taken into account to interpret the obtained charge values. The remaining charge, which must flow during the adsorption and condensation, is generally divided into a reorientation and a true adsorption part, as described in part 1.

The modeling of the surface processes requires also the consideration of the experimental conditions, such as the solution resistance and the final potential. Up to now the mostly applied kinetic models and, therefore, all kinetic parameters are obtained by modeling the well-known current shapes occurring at E_1. But it is well demonstrated in the simulations that the practice often used to subtract the exponentially decaying part from the entire current response to obtain the true condensation part in general is not correct. Exclusively for systems with high induction periods and low resistance, for example, the coumarine/H_2O system on mercury,[9,10] the real condensation process can be separated. The maximum in the total current response is often interpreted as the condensation itself. But in the physical picture presented here, the maximum in the total current response is due to the increasing adsorption rate on the condensed phase-free-surface. The increasing adsorption rate is caused by the increasing consumption of noncondensed molecules by the growing condensed islands. Therefore, the connection between the maximum in the current response and the condensation process is only indirect. The true condensation kinetics is represented by the nonmeasurable reorientation curve. The same considerations are valid for the transients obtained at the potential E_2 with the opposite sign. One proof for the correctness of the presented picture of the

coupled interplay between adsorption, double-layer charging, and condensation consists of the appearance of the transients obtained at the potential E_3 for low resistance. The interpretation of such shapes of transients with models in which the adsorption and condensation are considered independently of each other is not possible.

Summarizing, it can be said that the condensation kinetics can be clearly interpreted only for the following conditions and potentials, respectively:

(1) The condensation kinetics at the pit edges is slow compared with the adsorption and double-layer charging/discharging, or the induction period for nucleation is long, so that the maximum in the current response is clearly separated from the exponentially decaying part.

(2) In reorientation systems with very low resistances at the potential E_m the minimum in the current response represents the pure reorientation and, therefore, the condensation.

For all other conditions in the proximity of the middle of the pit region, the total current response includes parts of double-layer currents and adsorption currents.

Finally, it should be noted that the model analyzed here is valid for all chronoamperometric and chronocoulometric measurements in electrochemical systems. It is not restricted to two-dimensional phase-transition processes and can be easily adapted to other processes, for example for the interplay of double-layer charging with ordinary Langmuir kinetics or for the application of potential multistep methods.

List of Symbols

E_m, E'_m = potentials of maximum adsorption for systems without and with reorientation during the condensation process

E_{cp} = crossing point potential for systems with reorientation during the condensation process

c_{bulk} = bulk concentration of the organic molecules

k_a = effective rate constant of adsorption, $k_a = k_{ads}c_{bulk} + k_{des}$, with k_{ads} = adsorption rate constant and k_{des} = desorption rate constant

Γ_{max} = maximum possible surface concentration of the expanded adsorbate phase (corresponding to the hypothetical limit of $c_{bulk} \rightarrow \infty$)

Γ_{eq} = equilibrium concentration of the expanded adsorbate phase for given bulk concentration and double-layer potential, $\Gamma_{eq} = k_{ads}c_{bulk}\Gamma_{max}/(k_{ads}c_{bulk} + k_{des})$

Γ_{film} = surface concentration of the condensed adsorbate phase

Γ_a = surface concentration Γ of the adsorbate in the expanded phase, normalized to the film density: $\Gamma_a = \Gamma/\Gamma_{film}$

κ = ratio of $\Gamma_{max}/\Gamma_{film}$

δ = saturation concentration of the expanded adsorbate phase Γ_{sat}, normalized to the film density: $\delta = \Gamma_{sat}/\Gamma_{film}$

γ = normalized equilibrium adsorbate concentration, $\gamma = \Gamma_{eq}/\Gamma_{film}$

p_{dl} = dimensionless total periphery length of all islands of the condensed phase

Θ = surface coverage of the condensed phase (defined as the fraction of the film-covered surface area S_F with respect to the whole surface area S_0)

n_{dl} = dimensionless nucleation rate n_{dl}

k_n = preexponential nucleation rate constant

K = constant in the exponent of the nucleation law

k_w = rate constant of the linear growth of the condensed phase

α = dimensionless form of the effective rate constant of adsorption k_a

q_{sol}^{mol}, q_a^{mol}, q_{film}^{mol} = the partial double-layer charges per mole of adsorbate for the

solvent molecules, the molecules in the expanded phase, and the molecules in the condensed phase

q_{sol}, q_a, q_{film} = the partial double=layer charges per unit surface (surface charges) for surfaces completely covered with solvent molecules, molecules in the expanded phase, and molecules in the condensed phase, respectively

$q_{exp}(\Gamma_a)$ = surface charge of the expanded adsorbate phase

$C_0(E)$, $C_a(E)$, $C_{film}(E)$ = partial capacities per unit surface of the surface completely covered with solvent molecules, molecules in the expanded phase, and molecules in the condensed phase, respectively

$\bar{C}(E,\Theta,\Gamma_a)$ = mean capacity (per unit surface), representing the weighted sum of the partial capacities $C_0(E)$, $C_a(E)$ and $C_{film}(E)$