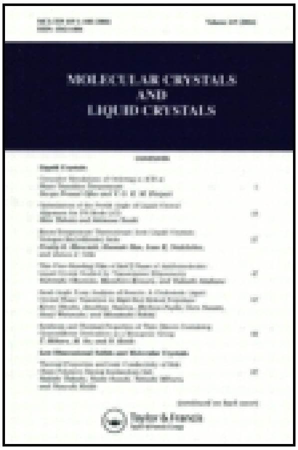

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F. C. M. Freire [a c], G. Barbero [a b], M. Scalerandi [a] & A. L. Alexe-Ionescu [a d]

[a] Dipartimento di Fisica del Politecnico, Corso Duca degli Abruzzi, Torino, Italia

[b] Instituto de Física, Universidade de São Paulo, São Paulo, SP - Brazil

[c] Departamento de Física - Universidade Estadual de MaringáColombo, Maringá, PR, Brazil

[d] Facultatea de Stiinte Aplicate, Universitatea Politehnica din Bucuresti, Splaiul Independentei, Bucuresti, Romania

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The Role of an Insulating Surface Layer on the Relaxation Time of the Ionic Redistribution in an Electrolytic Cell

F. C. M. Freire[1,3], G. Barbero[1,2], M. Scalerandi[1],
A. L. Alexe-Ionescu[1,4]
[1]Dipartimento di Fisica del Politecnico, Corso Duca degli Abruzzi,
Torino, Italia
[2]Instituto de Física, Universidade de São Paulo, São Paulo, SP - Brazil
[3]Departamento de Física - Universidade Estadual de Maringá,
Colombo, Maringá, PR, Brazil
[4]Facultatea de Stiinte Aplicate, Universitatea Politehnica din Bucuresti,
Splaiul Independentei, Bucuresti, Romania

We analyze the influence of a surface dielectric layer on the transient phenomena related to the ionic redistribution in an electrolytic cell submitted to a step-like external voltage. The adsorption-desorption phenomenon is taken into account in the famework of the Gouy-Chapman approximation, where the ions are assumed dimensionless. In the limit of small amplitude of the applied voltage, where the equations of the problem can be linearized, we obtain an analytical solution for the surface densities of ions, for the electrical potential and for the relaxation time for the transient phenomena. In the general case, when the linearized analysis is no longer valid, the solution of the problem is obtained numerically. The role of the thickness of the dielectric layer on the relaxation time is also discussed.

I. INTRODUCTION

To extract information about the physical parameters from measurements on electrolytic cells submitted to an external electric field, the theoretical models used for the interpretation of the experimental data have to take into account correctly the occurring transient effects [1,2]. Several studies have been indeed devoted to analyse the response of poorly conducting electrolytic cells to a step like potential [3–5], in the Gouy-Chapman approximation [6], in which the ions are assumed

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Address correspondence to F. C. M. Freire, Dipartimento di Fisica Del Politecnico, Corso Duca degli Abruzzi 24, Torino, 10129, Italy. E-mail: fernando.freire@polito.it

dimensionless. Such approximation is definitely valid for nematic liquid crystals, i.e., insulating materials for which the electrical conduction is mainly of ionic origin [7]. The aim of this contribution is to extend previous analyses by taking into account the adsorption phenomenon at the limiting surfaces, and also the presence of a surface dielectric layer deposited on the electrodes.

In order to simplify as much as possible the problem, we suppose that in the absence of an external field the liquid is locally and globally neutral. In this case, in the absence of an applied difference of potential, the electric potential in the cell is position independent, and the electric field zero. This hypothesis implies that the adsorption energy of the positive and negative ions with the limiting surfaces are the same. Since the adsorption energy can be identified with the electrostatic interaction energy of a given ion with its image in the substrate, the ions are supposed to have the same electrical charge, q, and geometrical dimension, ℓ [8,9]. As in [3] we assume furthermore that: 1) the ions are dispersed in an insulating isotropic liquid whose dielectric constant is ε; 2) the external voltage is a step of amplitude V_0 applied at $t=0$; 3) the electrodes are perfectly blocking, but they can adsorb ions; 4) the ionic mobilities of the positive and negative ions are identical, μ, as well as the diffusion coefficients, D; 5) the relation of Einstein $\mu/D = q/(K_B T)$, where K_B is the Boltzmann constant and T the absolute temperature is assumed valid; 5) the density of ions, in thermodynamical equilibrium, in the absence of limiting surfaces and external electric field, N, is supposed very small with respect to the density of the liquid. In this framework the recombination of the ions can be neglected.

Our analysis is mainly focused on the role of a surface dielectric layer on the ionic redistribution when the cell is submitted to an external electric field. In particular, the importance of this surface layer on the relaxation time will be investigated. The considered problem is of some importance in the display technology, where the surface insulating layer is deposited in order to avoid charge injection from the electrodes into the liquid crystal.

II. THEORETICAL BACKGROUND

Let us consider an electrolytic cell of thickness d (with dielectric constant ε) bounded by two identical dielectric layers of thickness h (and dielectric constant ε_h). We indicate by n_p and n_m the bulk densities of the positive and negative ions (p stands for plus and m for $-$), and by $\sigma_p(\pm d/2)$ and $\sigma_m(\pm d/2)$ the surface densities of positive and negative ions at the surfaces at $z = \pm d/2$.

In the absence of the external field and of the adsorbing surfaces $n_p = n_m = N$. When the surfaces are present and the external field is absent, due to the symmetries of the problem, we still have $n_p = n_m = n_{\mathrm{eq}}$, when the equilibrium has been reached. The bulk density n_{eq} is different from N since a part of the ions have been absorbed by the surfaces. In this condition, the surface densities of adsorbed ions are indicated by $\sigma_p = \sigma_m = \sigma_{\mathrm{eq}}$.

When the external field is applied, at $t = 0$, there is a migration of ions toward the electrodes. In this case, at equilibrium, $n_p(z,t) \to n_{p,\mathrm{eq}}(z), n_m(z,t) \to n_{m,\mathrm{eq}}(z), \sigma_p(\pm d/2,t) \to \sigma_{p,\mathrm{eq}}(\pm d/2)$, and $\sigma_m(\pm d/2,t) \to \sigma_{m,\mathrm{eq}}(\pm d/2)$. The phenomenon is governed by the equations of continuity for the two types of ions and by the equation of Poisson giving the actual electric potential profile when the ions are present.

The current density of ions is

$$j_r = -D\left(\frac{\partial n_r}{\partial z} \pm \frac{q n_r}{K_B T}\frac{\partial V}{\partial z}\right), \tag{1}$$

where $r = p, m$ and the sign is + for $r = p$ and − for $r = m$. The equation of continuity is

$$\frac{\partial n_r}{\partial t} = D\frac{\partial}{\partial z}\left(\frac{\partial n_r}{\partial z} \pm \frac{q}{K_B T} n_r \frac{\partial V}{\partial z}\right). \tag{2}$$

The equation of Poisson is [10]

$$\frac{\partial^2 V}{\partial z^2} = -\frac{q}{\varepsilon}(n_p - n_m). \tag{3}$$

We assume for the kinetic equation at the adsorbing surfaces that proposed by Langmuir [11,12]:

$$\frac{d\sigma_r}{dt} = k n_r - \frac{1}{\tau}\sigma_r, \tag{4}$$

where k is the adsorption coefficient, and τ a parameter, having the dimension of time, connected with the desorption phenomenon.

The boundary conditions for the ions density, in the presence of the adsorption phenomenon, are

$$j_r = \pm\frac{d\sigma_r}{dt}, \tag{5}$$

where the sign − is for $z = -d/2$, and + for $z = d/2$.

The boundary conditions for the potential have to take into account the presence of the dielectric layers. The difference of potential between the electrodes should be equal to the applied potential V_0

and the electric field has to satisfy the continuity equations at the electrolyte-dielectric layer interface:

$$\begin{aligned} V_0 &= -2hE_h(t) + \int_{-d/2}^{d/2} E(z,t)dz, \\ \varepsilon E(-d/2,t) &= \varepsilon_h E_h(t) + q\sigma, \end{aligned} \tag{6}$$

where $\sigma = \sigma_p - \sigma_m$ and $E_h(t)$ is the electric field inside the dielectric layer. Since free charges are not present within the dielectric layers, the electric field E_h is position independent. It follows that

$$\begin{aligned} V_h(t) = V(-d/2,t) &= -V_0/2 - hE_h(t) \\ &= -\frac{V_0}{2}\gamma + q\sigma\frac{h\gamma}{\varepsilon_h} \\ &\quad + q\frac{h\gamma}{d\varepsilon_h}\int_{-d/2}^{d/2} dz' \int_{-d/2}^{z'} n(z'',t)dz'', \end{aligned} \tag{7}$$

where $n = n_p - n_m$ and $\gamma = d\varepsilon_h/(d\varepsilon_h + 2h\varepsilon)$.

The initial conditions ($t = 0$) are

$$\begin{aligned} \sigma_{\text{eq}} &= \frac{1}{2}Nd\frac{1}{1 + d/(2k\tau)}, \\ n_{\text{eq}} &= N\frac{d/(2k\tau)}{1 + d/(2k\tau)}, \end{aligned} \tag{8}$$

for the surface and the bulk densities of ions, in the absence of the external electric field.

III. LINEAR ANALYSIS

A. Linearized Equations

We assume that the presence of a weak external electric field produces only a small perturbation on the distribution of ions (see Ref. [13] where the limit of such assumption is discussed). By defining $n_r(z,t) = n_{\text{eq}} + \delta n_r(z,t)$, and $\sigma_r(t) = \sigma_{\text{eq}} + \delta\sigma_r(t)$, where $\delta n_r(z,t) \ll n_{\text{eq}}$, it follows that Eqs. (2) and (3) can be linearized as

$$\frac{\partial(\delta n_r)}{\partial t} = D\frac{\partial}{\partial z}\left(\frac{\partial(\delta n_r)}{\partial z} \pm \frac{q}{K_B T}n_{\text{eq}}\frac{\partial V}{\partial z}\right), \tag{9}$$

$$\frac{\partial^2 V}{\partial z^2} = -\frac{q}{\varepsilon}(\delta n_p - \delta n_m), \tag{10}$$

The boundary conditions are

$$D\left(\frac{\partial(\delta n_r)}{\partial z} \pm \frac{q}{K_B T} n_{\mathrm{eq}} \frac{\partial V}{\partial z}\right) = k\delta n_r(t) - \frac{1}{\tau}\delta\sigma_r, \tag{11}$$

$$-D\left(\frac{\partial(\delta n_r)}{\partial z} \pm \frac{q}{K_B T} n_{\mathrm{eq}} \frac{\partial V}{\partial z}\right) = k\delta n_r(t) - \frac{1}{\tau}\delta\sigma_r, \tag{12}$$

for $z = -d/2$ and for $z = d/2$, respectively.

To find the solution, we separate the unknowns of our analysis in transient and equilibrium (for $t \to \infty$) components as $\delta n_r(z,t) = \delta n_r^t(z,t) + \delta n_r^e(z), V(z,t) = V^t(z,t) + V^e(z)$, and $\delta\sigma_r(\pm d/2, t) = \delta\sigma_r^t(\pm d/2, t) + \delta\sigma_r^e(\pm d/2)$. We consider here only the solutions for the transient components. For the equilibrium components the results are reported elsewhere [4].

B. Relaxation of the Transient Components

We look for the solutions of the bulk Eqs. (9,10) for the transient components of the form:

$$\delta n_r^t(z,t) = \psi_r(z)e^{-at}, \qquad V^t(z,t) = \phi(z)e^{-at}, \tag{13}$$

where $a > 0$, since the solutions have to vanish for $t \to \infty$. By taking into account Eq. (13), from the kinetic equation at the interface

$$\frac{d\delta\sigma_r^t(t)}{dt} = k\delta n_r^t(t) - \frac{1}{\tau}\delta\sigma_r^t(t), \quad \text{for } z = \pm d/2, \tag{14}$$

we obtain

$$\delta\sigma_r^t(t) = M_\pm e^{-t/\tau} + \frac{k\tau}{1 - a\tau}\psi_r(\pm d/2)e^{-at}, \tag{15}$$

where $M_\pm$ are integration constants to be determined by the boundary conditions. By substituting Eqs. (13) and (15) into Eqs. (11,12) written for the transient components, we obtain

$$\begin{aligned}
\left(\psi_r' \pm \frac{qn_{eq}}{K_B T}\phi'\right)e^{-at} &= -\frac{k}{D}\frac{a\tau}{1 - a\tau}\psi_r e^{-at} - \frac{1}{D\tau}M_- e^{-t/\tau}, \\
\left(\psi_r' \pm \frac{qn_{eq}}{K_B T}\phi'\right)e^{-at} &= \frac{k}{D}\frac{a\tau}{1 - a\tau}\psi_r e^{-at} + \frac{1}{D\tau}M_+ e^{-t/\tau},
\end{aligned} \tag{16}$$

for $z = -d/2$ and $z = d/2$, respectively. From Eqs. (16), which have to be valid for all t, it follows that $M_+ = M_- = 0$.

From Eqs. (9,10), by taking into account the symmetry of the problem, we get

$$\psi_r(z) = \pm B_1 \sinh(\nu_1 z) + B_3 \sinh(\nu_3 z), \tag{17}$$

$$\phi(z) = A_1 z - \frac{2q}{\varepsilon \nu_1^2} B_1 \sinh(\nu_1 z), \tag{18}$$

where

$$\nu_1 = (1/\lambda_{\mathrm{eq}})\sqrt{1 - (a/D)\lambda_{\mathrm{eq}}^2}, \quad \text{and} \quad \nu_3 = i\sqrt{a/D}. \tag{19}$$

The boundary condition for the potential is

$$\phi(-d/2, t)e^{-at} - V^e(-d/2) = V_h(t). \tag{20}$$

Substituting Eq. (18) into Eq. (20) we obtain

$$A_1 = \frac{2B_1}{d}\left[-\frac{2q}{\varepsilon \nu_1^2} X_d - \frac{2qk\tau}{1 - a\tau}\frac{h\gamma}{\varepsilon_h} X_d + \frac{2qh\gamma}{d\varepsilon_h}\left(\frac{2X_d}{\nu_1^2} + \frac{dY_d}{\nu_1}\right)\right],$$

where $X_d = -\sinh(d/(2\lambda_{\mathrm{eq}}))$ and $Y_d = \cosh(d/(2\lambda_{\mathrm{eq}}))$.

By imposing the boundary conditions (16), we obtain $B_3 = 0$ and

$$\begin{aligned}&\left(1 - \frac{ka\tau}{D(1 - a\tau)}\nu_1^2\lambda_{\mathrm{eq}}^2 \frac{d}{2} + \frac{h\gamma\varepsilon}{d\varepsilon_h}\left(\frac{dk\tau\nu_1^2}{1 - a\tau} - 2\right)\right)\\ &\quad = \coth\left(-\nu_1 \frac{d}{2}\right)\left(-1 + \nu_1^2\lambda_{\mathrm{eq}}^2 + \frac{2h\gamma\varepsilon}{d\varepsilon_h}\right)\upsilon_1 \frac{d}{2},\end{aligned} \tag{21}$$

which is the eigenvalues equation of the present problem.

It follows that the solution of the problem is given by the superposition of functions of the form of Eqs. (13) with the acceptable values of ν_1, given by the eigen-values Eq. (21). The first solution is easily found to be $\nu_1 = 0$, which means $a = \lambda_{\mathrm{eq}}^2/D$. However, this solution is not interesting because it corresponds to a case in which there is not separation of charges. More important are the other solutions, which can be found numerically. Note that also solutions with t_d smaller than τ, which is the typical time scale of the adsorption events, are not interesting. In fact, the transient phenomenon in the bulk cannot be faster than the adsorption phenomenon at the limiting surfaces.

IV. RESULTS AND DISCUSSION

We consider here an electrolytic cell of thickness $d = 25\,\mu\mathrm{m}$ bounded by two dielectric layers of thickness h (varied in the numerical calculations). We assume monovalent ions, with density $N = 4.2 \times 10^{20}\,\mathrm{m}^{-3}$

in thermodynamical equlibrium, and diffusion coefficient $D = 8.2 \times 10^{-12}\,\mathrm{m}^2/\mathrm{s}$. The temperature is $T = 300\,\mathrm{K}$. The cell has dielectric constant $\varepsilon_h = 6.7\varepsilon_0$, and the one of the surface layer is $\varepsilon_h = 2.1\varepsilon_0$. The parameters correspond to a commercial liquid crystal [14]. We assume that the adsorption occurs at the surfaces separating the cell from the dielectric layer, with $k = 10^{-6}\,\mathrm{m/s}$ and $\tau = 0.01\,\mathrm{s}$, unless otherwise specified. Furthermore, the potential V_0 is chosen in the range from 0.1 mV to 25 mV.

The analytical solutions are found using the linearized analysis reported in the previous Section. Since linearization is valid only when the applied potential is small, we have also performed numerical simulations to study the dynamics of the system. Details about the numerical solution can be found elsewhere [15,16].

The response of the system to a step-like potential consists in a transient component which decays exponentially towards an equilibrium state. We plot the time evolution of $n_p(\zeta, t)$ in $\zeta = -d/2 + l/2$, where $l = 0.05\,\mu\mathrm{m}$ is the space step used in the simulation in Figure 1. The applied potential causes the accumulation of ions close to the surface, which is responsible for the generation of an electric field opposite to the applied one. As a consequence, the electrical potential in the bulk diminishes with increasing time, as shown in Figure 2. The increase of h corresponds to a larger accumulation of adsorbed ions. As a result the density of ions in the bulk is diminished and the potential decays

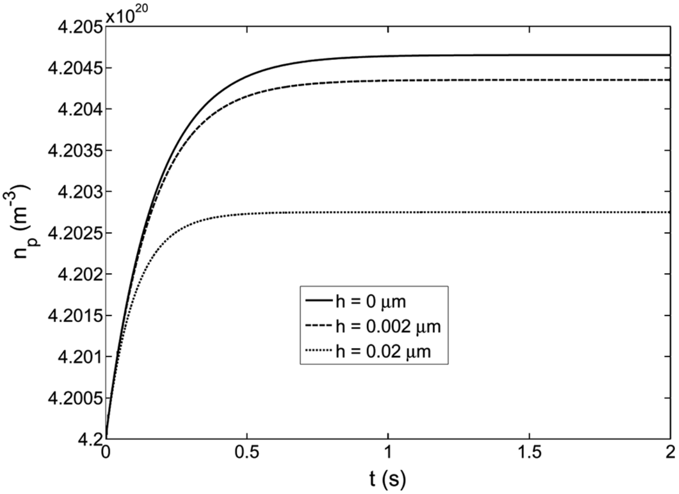

FIGURE 1 Density of positive ions close to the surface, at $z = -d/2 + l/2$, vs. time for three values of h. The applied potential is $V_0 = 0.1\,\mathrm{mV}$.

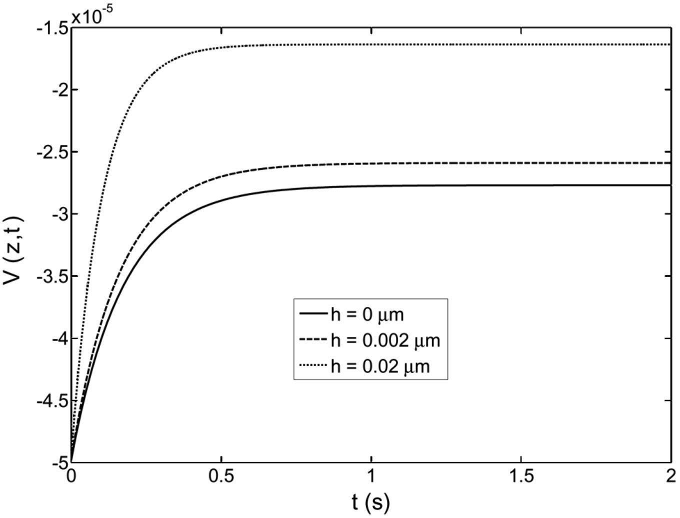

FIGURE 2 Electrical potential close to the surface, at $z = -d/2 + l/2$ vs. time for three values h. The applied potential is $V_0 = 0.1\,\mathrm{mV}$.

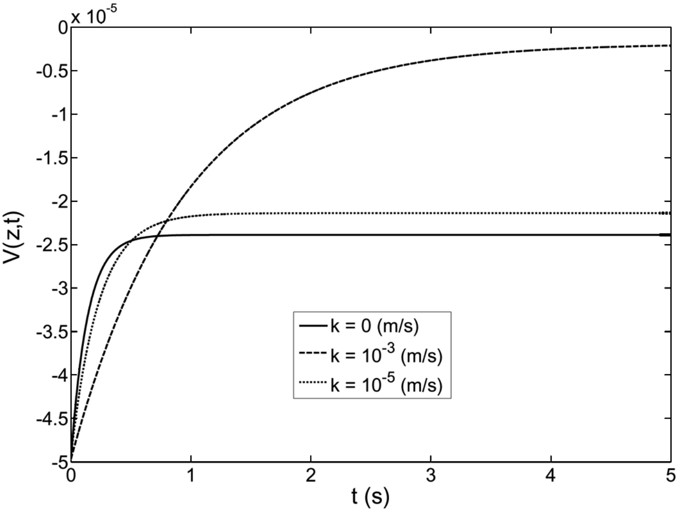

FIGURE 3 Electrical potential close to the surface, at $z = -d/2 + l/2$, vs. time for three values of adsorption parameters k, and $h = 0$. The figure corresponds to $V_0 = 0.1\,\mathrm{mV}$ and $\tau = 10^{-2}\,\mathrm{s}$.

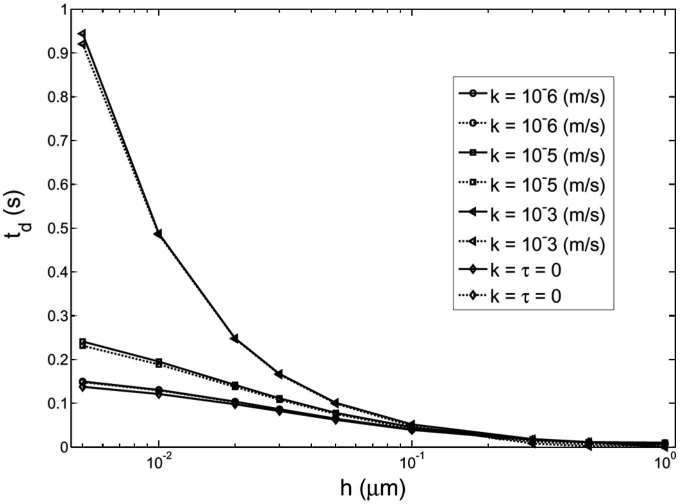

FIGURE 4 Decay time as a function of h for different values of the adsorption parameters. Comparison between analytical (solid-line) and numerical (dot-line) solutions. For the case $k = 0$ the analytic and numerical curves coincide perfectly for small values of h. The figure corresponds to $\tau = 10^{-2}\,$s.

faster. This is confirmed form the results reported in Figure 3, where the potential as a function of time is considered for different values of the adsorption parameter k, and $h = 0$. Increasing k corresponds to a stronger role of adsorption, with results similar to that obtained when increasing h, both for what concerns the larger decay of the potential in the bulk and for the diminished concentration of ions. On the contrary, the decay time, which was decreasing with increasing h, now is increasing for increasing k. Finally, in Figure 4, the decay time is reported as a function of h for $V_0 = 0.1\,$mV and different values of the adsorption parameters (as reported in the plot). The decay time is sensitive to the adsorption parameters only for low values of the dielectric layer thickness. Increasing h, the adsorption phenomenon becomes less and less important for the determination of the transient solution. Also, the agreement between the numerical and the analytical solutions becomes poorer with increasing h and/or with increasing the adsorption parameters.

V. CONCLUSION

We have investigated the ionic redistribution occurring in an electrolytic cell submitted to an external electric field. In our analysis we have considered the influence of the adsorption at the interfaces as well as the role of a surface insulating layer deposited on the electrodes on the transient phenomena. Our analysis has been performed in the framework of the Gouy-Chapman approximation, where the ions are assumed dimensionless. For the set of physical parameters considered, in the limit of small applied voltage, we are far from the problems connected with the unphysical increasing of the surface density of the ions close to the electrodes, requiring the introduction of the layer of Stern, related to the finit dimension of the ions. Hence, our analytical predictions are expected to work well for applied voltages smaller than (or of the order of) the thermal electrical voltage $V_T = K_B T/q \sim 25\,\mathrm{mV}$ for monovalent ions.

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