The kinetics of mercury nucleation from Hg$_2^{2+}$ and Hg$^{2+}$ solutions on vitreous carbon electrodes

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Abstract

The kinetics of the electrochemical nucleation of Hg onto vitreous carbon were studied from analysis of potentiostatic current transients obtained at different overpotentials in Hg$_2^{2+}$ and Hg$^{2+}$ solutions. Similar sizes of critical nuclei and number densities of sites on the surface were found for nucleation of Hg from both solutions, indicating, in agreement with nucleation theory, that the rates of nucleation are controlled by surface energies and deposit–substrate interactions. Saturation number densities of nuclei were deduced from the kinetic analysis, and their relationship with those obtained from direct observation of the electrode surface is discussed. It was found that at low overpotentials, the nuclei deposited from both solutions were uniformly distributed on the electrode surface, whereas their distribution was affected by inhibition of the nucleation rates close to already established nuclei at high overpotentials. This inhibition was enhanced during deposition from Hg$^{2+}$ solution. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The kinetics of three-dimensional nucleation followed by diffusion-controlled growth of nuclei has been the subject of numerous studies (see, e.g. Ref. [1] and references therein). The steady-state nucleation rates, and the number density of nucleation sites on the surface, may be obtained from current transients following potential steps [2–5], although these are distributed quantities due to dispersion of the energies of sites throughout the surface [6] and to variations in concentration and overpotential in the vicinity of growing nuclei [7], leading to saturation of the surface with nuclei, with characteristic spatial distributions [8–11].

In spite of the developments in the understanding of the physical aspects of electrocrystallization processes, the effects of variables affecting the chemical state of the electrodepositing species on the kinetics of electrochemical nucleation processes have not been explored in detail. Some studies have been carried out on the effects of the nature of the supporting electrolyte and the coordination sphere of electroactive species on the kinetics of electrocrystallization [12–15] but, to our knowledge, detailed experimental studies of the kinetics of the electrochemical nucleation of a metallic phase M from its ions M$^{z+}$ in different oxidation states, which is the aim of this work, have not been conducted. The main reason that led us to consider the nucleation of mercury from solutions of Hg$_2^{2+}$ or Hg$^{2+}$ ions for this study is that the standard potential for Hg$_2^{2+}$ reduction to Hg, 0.7960 V, is more negative than that of Hg$^{2+}$ to Hg, 0.8535 V [16], allowing, in principle, the direct reduction of both ions –especially Hg$^{2+}$– to Hg. The equilibria involving the Hg, Hg$_2^{2+}$ and Hg$^{2+}$ species

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constrain such a simple analysis but, as shown in this paper, the variation of the nucleation rates with the oxidation state of the electrodepositing species is thoroughly consistent with electrochemical nucleation theory and, particularly, with the predictions of the classical work of Erdey–Gruz and Volmer [17].

2. Experimental

A three-electrode, two-compartment cell was used throughout. The bottom of the main compartment was an optical flat in order to allow the in situ microscopic observation of the surface of the working electrode during the electrodeposition process, using an inverted stage microscope (Union Versamet 2) and a video camera (COHU 4815), connected to a frame grabber (Imaging Technology PCvision Plus) in a PC to acquire, analyse and display in a video monitor images of the electrode surface. The working electrode was a vitreous carbon (Electrosynthesis GC-30) disc of 0.0707 cm² area, sealed to glass, polished to a mirror finish. The counter electrode was a platinum ring encircling the working electrode near the bottom of the cell. Mercury in contact with the working solution, but located in a separate compartment connected to the main cell through a Luggin capillary, was used as the reference electrode; the potential differences applied between working and reference electrodes were thus taken as the overpotentials for the electrodeposition reactions, and all overpotentials are reported with respect to the reference electrodes used. The experiments were carried out with an EG&G PAR 273 potentiostat under EG&G M270 software.

Mercury electrodeposition were studied from 0.01 mol dm⁻³ aqueous solutions of the mercury (I) or (II) nitrates, respectively, containing also 1 mol dm⁻³ KNO₃ as supporting electrolyte, acidified with a few drops of HNO₃ to avoid hydrolysis of Hg₂⁺ or Hg²⁺. All solutions were prepared with analytical grade reactants and ultra-filtered distilled water. Cyclic voltammetry was used to verify the electrochemical behaviour of the electrode in each solution and to determine the faradaic efficiencies of the respective electrodeposition reactions. The kinetics of nucleation were studied under potentiostatic conditions. Very large dispersion of the data was found during Hg deposition from Hg₂⁺ solutions at cathodic overpotentials lower than 200 mV. Thus the kinetics of nucleation from mercury (I) solution were studied with single potential steps between +150 mV versus Hg²⁺/Hg and 190 ≤ −η ≤ 320 mV. Deposition from mercury (II) solution were studied with steps from +150 mV versus Hg²⁺/Hg to 160 ≤ −η ≤ 300 mV. In each case, the corresponding current transient and an image of the electrode surface with the electrodeposited nuclei upon completion of the nucleation process were acquired. Between experiments, nuclei were dissolved with positive potential pulses in the working solution, followed by immersion of the electrode surface in an aqueous solution containing 1% NaCN and 6% H₂O₂, and rinsing with ultra-filtered distilled water.

2.1. Analysis of current transients

The nucleation rate, A, and the number density of nucleation sites, N₀, were obtained from the chronocoulometric maxima [2]. Assuming that nucleation is excluded within regions of reduced supersaturation around growing nuclei, and that the radii of these zones of exclusion for nucleation are given by rₑ = (kD/t)¹/², where k = (8πeM/ρ)¹/², e is the bulk concentration of electrodepositing species, D is the diffusion coefficient in solution, M is its molar mass, ρ is the density of the deposit, and t is the age of the growing nuclei, then the saturation number density of nuclei, Nₛ, was estimated from the A and N₀ values obtained from analysis of current transient maxima as

\[ Nₛ = AN₀ \int_0^t \exp[-N₀πkD(Au - 1 - e^{-Au}/A)]e^{-Au} du \]

For the particular case of ‘progressive’ nucleation, i.e. when nucleation occurs at a low rate on a very large number density of nucleation sites, it may be shown [18] that \( Nₛ = (AN₀/2kD)^{1/2} \). In the general case, however, a closed form solution of the integral in Eq. (1) is not known, and thus \( Nₛ \) was obtained from the numerical evaluation of Eq. (1). The \( Nₛ \) values obtained were invariably lower than those corresponding to the particular case of ‘progressive’ nucleation. The values of \( Nₛ \) thus obtained were then compared with those obtained from the direct analysis of microscope images, \( Nₘₙ \).

2.2. Analysis of images

Experimental details about the methods used for image analysis have been reported elsewhere [10]. Square segments of the electrode surface of 4.00 × 10⁻⁴ cm² were analysed from images of the surface obtained after each of the experiments. The relative location of each nucleus was established with the aid of a cursor on the image of the electrode surface, using Jandel Scientific Java software. These data were later used to obtain the nearest neighbour distributions [9], and the microscopically determined saturation number densities, \( Nₘₙ \), of electrodeposited nuclei on the electrode surface.
3. Results and discussion

3.1. Faradaic efficiencies for mercury electrodeposition from Hg$^{2+}_3$ and Hg$^{2+}_5$ solutions

Fig. 1(a) shows the voltammetric response of the vitreous carbon electrode in Hg$^{2+}_3$ solution. The characteristic loop due to phase formation phenomena [19,20] indicates nucleation and growth of Hg starting at ca. −220 mV, followed by a cathodic peak at ca. −320 mV, and the anodic stripping of electrodeposited mercury during the positive sweep, with a peak at ca. 70 mV. The ratio of anodic stripping and cathodic deposition charges, $q_d/q_c$, yields the faradaic efficiency of the electrodeposition process. This was found to be 0.91 ± 0.03 during mercury deposition from Hg$^{2+}_3$, indicating that the cathodic current is almost entirely consumed by the formation and growth of mercury nuclei.

The voltammetric response in Hg$^{2+}_5$ solution is shown in Fig. 1(b). In contrast to that obtained in Hg$^{2+}_3$ solution, reduction to Hg commences at ca. −160 mV and the cathodic peak occurs at ca. −230 mV, i.e. at somewhat lower overpotentials than in Hg$^{2+}_3$ solution. The difference of overpotentials for mercury deposition upon reduction of Hg$^{2+}_3$ or Hg$^{2+}_5$ ions is unrelated to the difference between the standard potentials of the Hg$^{2+}_3$/Hg and Hg$^{2+}_5$/Hg couples, 0.7960 and 0.8535 V, respectively [16], since the working electrode has been polarised directly with reference to the equilibrium potential of mercury in contact with its ions in solution. In spite of the mechanistic complications discussed below, this result suggests that mercury nucleation occurs more readily from Hg$^{2+}_5$ than from Hg$^{2+}_3$ solutions. Furthermore, the supersaturation $c/c^*$ ratio at the metal | metal ion electrode is given by [21] $\exp(\gamma F \eta /RT)$, where $\gamma F$ is the molar charge transferred during the electrodeposition process and $\eta$ is the overpotential, from which it follows that the Gibbs energy of formation of a hemispherical critical nucleus is given by (see, e.g. Refs [17,22])

$$\Delta G^* = (16\pi \gamma^3 M^2/3\rho z^2 F^2\eta^3)\phi(\theta)$$ (2)

where $\gamma$ is the interfacial tension at the deposit | solution interface, $M$ is the molar mass of the electrodepositing species, $\rho$ is the density of the deposit, and $\phi(\theta) = (2 - 3 \cos \theta + \cos^2 \theta)/4$, where $\theta$ is the contact angle between the nucleus and the substrate ($\phi(\theta) = 1/2$ for a hemisphere). The nucleation rate can be expressed as

$$A = A_0 \exp(-\Delta G^*/kT)$$

$$= A_0 \exp[-16\pi \gamma^3 M^2 \phi(\theta)/3\rho z^2 F^2\eta^3 kT]$$ (3)

The molar charge for mercury deposition from Hg$^{2+}_5$ solution is twice as large as from Hg$^{2+}_3$, hence the reversible work of nucleus formation is four times lower and, consequently, the nucleation rate is considerably higher.

The other important difference between the results shown in Fig. 1(a) and (b) is in the respective current efficiencies for mercury deposition. Whereas this was invariably close to unity during reduction of Hg$^{2+}_3$, it depended on the conditions of the voltammetric experiment during mercury deposition from Hg$^{2+}_5$, being only 0.48 under the conditions of Fig. 1(b). Table 1 shows the faradaic efficiencies obtained from voltammetric cycles at 50 mV s$^{-1}$ with various negative potential limits. Mercury deposition occurs during longer times as the negative potential limit is increased, with the electrodeposited droplets attaining larger sizes. Inferring that Hg$^{2+}_3$ is produced during reduction of Hg$^{2+}_5$ to Hg at the mercury | solution interface, then the diminished faradaic efficiencies found upon sweep reversal at less negative potentials may arise from the more efficient mass transfer of Hg$^{2+}_3$ ions to the bulk from smaller droplets, due to the locally spherical symmetry. Two processes may account for the production of Hg$^{2+}_3$ during reduction of Hg$^{2+}_5$:

(i) Two-step Hg$^{2+}_5$ reduction

![Fig. 1. Cyclic voltammetry of vitreous carbon in 0.01 mol dm$^{-3}$ Hg$_2$(NO$_3$)$_2$ (a) and 0.01 mol dm$^{-3}$ Hg(NO$_3$)$_2$ (b) solutions in the presence of 1 mol dm$^{-3}$ KNO$_3$, at a sweep rate of 50 mV s$^{-1}$.](image_url)
(ii) A well defined reversible $2e^-$ voltammetric reduction peak at low sweep rate, becoming irreversible at higher sweep rates [28]. A single reduction wave was observed with rotating disc electrodes on deposit-free surfaces, but two on electrodes partially covered with mercury, the first due to the irreversible reduction of $\text{Hg}_2^{2+}$ produced by disproportionation, cf. Eq. (7), and the second, at much more negative potential, associated with the direct $2e^-$ reduction of $\text{Hg}^{2+}$. (iii) Two reduction waves at high pH [27], the first due to reduction of $\text{Hg}^{2+}$ and the second corresponding to the reduction of $\text{HgOH}^+$ and/or $\text{Hg(OH)}_2^{+}$, with detection of $\text{Hg}_2^{2+}$ at the ring in rotating ring-disc experiments only during the second reduction wave, augmented with pH due to the increased formation of $\text{Hg(OH)}_2$. Thus the various faradaic efficiencies found for mercury electrodeposition from $\text{Hg}^{2+}$ under diverse conditions, together with the literature data, indicate the involvement of $\text{Hg}_2^{2+}$, either as reaction intermediate or as a disproportionation product.

### 3.2. Nucleation kinetics

Families of current transients obtained at diverse overpotentials during mercury electrodeposition from 0.01 mol dm$^{-3}$ $\text{Hg}_2^{2+}$ and 0.01 mol dm$^{-3}$ $\text{Hg}^{2+}$ solutions are shown in Figs. 2 and 3, respectively. The currents first rise due to the formation and growth of mercury droplets on the surface, decreasing at longer times and approaching that due to semi-infinite diffusion to a planar surface, described by the well known Cottrell equation. The growth rate of the deposit is then controlled by the transport of electrodepositing species from the bulk of solution to the surface of the growing mercury droplets. The diffusion coefficients were determined from the current transients with $I$ versus $t^{1/2}$ Cottrell plots, and also using a rotating disc electrode with $I$ versus $\omega^{1/2}$ Levich plots. Diffusion coefficients of $1.2 \times 10^{-5}$ and $1.4 \times 10^{-5}$ cm$^2$ s$^{-1}$ were found for $\text{Hg}^{2+}$ and $\text{Hg}^{2+}$, respectively, and used for the evaluation of $A$, $N_0$ and $N_{si}$, as described in the experimental section.

Fig. 4 shows the nucleation rates as a function of overpotential for mercury electrodeposition from both solutions. The rates of mercury nucleation from $\text{Hg}^{2+}$ solutions increase continuously with overpotential and are invariably faster than the corresponding rates in $\text{Hg}_2^{2+}$. The latter, showing large dispersions up to 0.25 V, increase with the overpotential at higher values. According to Eq. (3), the nucleation rates are represented as $\ln(\Delta)$ versus $1/\eta^2$ in Fig. 5, yielding linear plots with ca. four times lower slope for deposition from $\text{Hg}^{2+}$ ($-0.18$ V$^2$) as compared with $\text{Hg}_2^{2+}$ ($-0.73$ V$^2$), as expected from the twice larger molar charge...
needed. From these slopes and Eq. (3), and considering from extrapolation of electrocapillary data [29] that \( \gamma \) is ca. 300–350 mN m\(^{-1}\) at the Hg\(^{2+}\)/Hg and Hg\(^{2+}\)/Hg deposition potentials, it follows that \( \phi(\theta) \) is ca. 0.4, i.e. that the contact angle at the vitreous carbon | mercury interface is about 70°, with a number of atoms in

critical nuclei varying from 7 to 1 as the overpotential increases from 150 to 300 mV. Given the small size of the critical clusters, the good agreement obtained with classical theory is remarkable, and the number of atoms in the critical nuclei is best evaluated [31] from the slopes of the \( \ln (A) \) versus \( \eta \) plots shown in Fig. 4. Thus, taking \( \alpha = 0.5 \) for mercury deposition from Hg\(^{2+}\), and \( \alpha = 0.33 \) [30] from Hg\(^{2+}\), yields in both cases that single atoms adsorbed onto active sites on the surface act as critical nuclei and grow irreversibly. Further research on the physical quantities describing small clusters [32] is needed for a more detailed analysis of nucleation kinetics at high supersaturations.

The number densities of nucleation sites on the surface are shown in Fig. 6 for deposition from both Hg\(^{2+}\) and Hg\(^{2+}\) solutions. In spite of the large dispersion of the low overpotential data in Hg\(^{2+}\) solution, it was found that at a given overpotential, nucleation of mer-

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Fig. 3. Current transients recorded during mercury electrodeposition on to vitreous carbon from 0.01 mol dm\(^{-3}\) Hg\(^{2+}\) in 1 mol dm\(^{-3}\) KNO\(_3\) at the overpotentials indicated, in mV.

Fig. 4. Rates of mercury nucleation on vitreous carbon from 0.01 mol dm\(^{-3}\) Hg\(^{2+}\) (○) and 0.01 mol dm\(^{-3}\) Hg\(^{2+}\) (△) as a function of the overpotential.

Fig. 5. Plot of the logarithm of the nucleation rate as a function of \( 1/\eta^2 \), for mercury deposition from 0.01 mol dm\(^{-3}\) Hg\(^{2+}\) (○) and 0.01 mol dm\(^{-3}\) Hg\(^{2+}\) (△).

Fig. 6. Number densities of nucleation sites on the vitreous carbon surface, obtained from analysis of current transients recorded during mercury deposition from 0.01 mol dm\(^{-3}\) Hg\(^{2+}\) (○) and 0.01 mol dm\(^{-3}\) Hg\(^{2+}\) (△), as a function of the overpotential.
The saturation number densities of nuclei, \( N_{si} \), obtained from analysis of current transients recorded during deposition of Hg from both solutions are represented as a function of the overpotential in Fig. 7. The nuclear number densities attained upon deposition from \( \text{Hg}^{2+} \) solution were higher than from \( \text{Hg}^{2+} \), although with a lower rising slope with \( \eta \). The nuclear number densities were also determined from analysis of images of the electrode surface obtained after potential pulses, \( N_{sm} \), and these are shown in Fig. 8. They also show larger number densities of nuclei deposited from \( \text{Hg}^{2+} \) but, in contrast to the plots of ln \( (N_{si}) \) versus \( \eta \) shown in Fig. 7, the ln \( (N_{sm}) \) versus \( \eta \) plots show comparable slopes. Fig. 9 shows the correlation between the \( N_{si} \) values obtained by analysis of current transients, \( N_{si} \), and microscope images, \( N_{sm} \), after Hg deposition from both solutions, assuming that the radii of zones of exclusion for nucleation are given by \( r_e = (kD\tau)^{1/2} \). In both \( \text{Hg}^{2+} \) and \( \text{Hg}^{2+} \) solutions, analysis of current transients yielded values of \( N_{si} \) that were consistently smaller than the \( N_{sm} \) values obtained from micrographs. The discrepancy between the chronoamperometrically and microscopically determined values of \( N_{si} \) indicates that the inhibition of nucleation in the vicinity of growing nuclei is overestimated with exclusion zones with radii \( r_e \) as assumed in our analysis. A more realistic treatment of nucleation inhibition should consider the distribution of the stationary nucleation rates around growing nuclei [33,34].

3.3. Spatial distribution of mercury nuclei

Probability densities of nearest neighbour distributions of electrodeposited mercury nuclei were obtained from micrographs of the electrode surface and are shown in Figs. 10 and 11 for mercury deposition from \( \text{Hg}^{2+} \) and \( \text{Hg}^{2+} \) solutions, respectively. As observed in other previously studied systems [10,14], mercury nuclei deposited from either \( \text{Hg}^{2+} \) or \( \text{Hg}^{2+} \) solution at low overpotentials were uniformly distributed on the electrode surface, whereas their distribution was affected by inhibition of the nucleation rate close to already established nuclei [7,9,34] at high overpotentials. A quantitative comparison of the experimental spatial distributions with those obtained from simulations and the theoretical random distribution may be carried out with statistical criteria [35], such as the non-dimensional ratio \( \sigma / \langle r \rangle \), where \( \langle r \rangle \) is the mean distance between nearest neighbours and \( \sigma \) is the standard deviation of the nearest neighbour distances from the mean. For uniformly distributed nuclei on the electrode surface...
\[ \langle r \rangle = 1/(2N_s^{1/2}) \] and \[ \sigma = [(4 - \pi)/4\pi N_s]^{1/2}, \] thus \[ \sigma/\langle r \rangle = [((4 - \pi)/\pi)^{1/2} = 0.523. \] Nucleation inhibition close to already established nuclei introduces order in the spatial distribution, reducing the \( \sigma/\langle r \rangle \) ratio. Fig. 12 shows \( \sigma/\langle r \rangle \) of the distributions of distances between nearest neighbours deposited from \( \text{Hg}^{2+} \) and \( \text{Hg}^{2+} \) solutions at different overpotentials. In Fig. 12, the horizontal lines indicate the \( \sigma/\langle r \rangle \) values corresponding to different conditions. Line (a) corresponds to the random, uniform distribution, as described above. The value represented by (b), \( \sigma/\langle r \rangle = 0.317, \) was obtained from simulations considering nucleation exclusion within a circle of radius \( r_e = qu^{1/2} \) around each established growing nucleus [9], where \( q \) is constant and \( u \) is the age of the nucleus. The value of (c), \( \sigma/\langle r \rangle = 0.321, \) was obtained from simulations considering nucleation inhibition by the most influential neighbour [34], with the nucleation rate at a distance \( r \) from the centre of a growing nucleus given by \( A(r,u) = A_\infty (1 - qu^{1/2}/r), \) where \( A_\infty \) is the uninhibited nucleation rate sufficiently far from the nucleus. The \( \sigma/\langle r \rangle \) values obtained from either set of simulations are nearly indistinguishable and corroborate, as discussed elsewhere [34], that very similar spatial distributions arise from consideration of exclusion or inhibition by the most influential neighbour. Fig. 12 also indicates that the experimentally obtained \( \sigma/\langle r \rangle \) values decrease with the overpotential.

**Fig. 10.** Normalised probability densities of the nearest neighbour distances for mercury nuclei deposited from 0.01 mol dm\(^{-3}\) \( \text{Hg}^{2+} \) solution at 220 (a) and 260 (b) mV. The number of nuclei in \( 4 \times 10^{-4} \) cm\(^2\) of surface was 101 (a) and 265 (b). Also shown are the probability densities for uniformly distributed nuclei (---) and with nucleation exclusion within \( r_e = qu^{1/2} \) (—), see text.

**Fig. 11.** Normalised probability densities of the nearest neighbour distances for mercury nuclei deposited from 0.01 mol dm\(^{-3}\) \( \text{Hg}^{2+} \) solution at 170 (a), 220 (b) and 300 (c) mV. The number of nuclei in \( 4 \times 10^{-4} \) cm\(^2\) of surface was 232 (a), 895 (b) and 3792 (c). Also shown are the probability densities for uniformly distributed nuclei (---) and with nucleation exclusion within \( r_e = qu^{1/2} \) (—), see text.
i.e. that the distributions depart from uniform as $\eta$ increases. For Hg deposition from Hg$_2^{2+}$ solution, the $\sigma/\langle r \rangle$ values tend to converge at sufficiently high overpotentials towards those given by the simulations, in accordance with results already reported for the electrodeposition of Pb from Pb$_2^{2+}$ [10] and Ag from Ag(NH$_3$)$_2^{+}$ [14] solutions. In contrast, the spatial distributions of Hg nuclei electrodeposited from Hg$_2^{2+}$ solution attain values of $\sigma/\langle r \rangle$ significantly lower than 0.32 at sufficiently high overpotentials, thus departing from the uniform distribution further apart than expected from the inhibitory effects considered by the simulations. This is also manifest from the probability densities of the nearest neighbour distributions of Hg deposited from Hg$_2^{2+}$ at high overpotentials, such as that shown in Fig. 11(c), which are steeper and narrower than that obtained from simulation.

3.4. The role of Hg$_2^{2+}$ during Hg nucleation from Hg$_2^{2+}$ solution

It is thus apparent, from the higher nuclear number densities and their more ordered spatial distributions, that the Hg$_2^{2+}$ ions produced during reduction of Hg$_2^{2+}$ are also involved in the nucleation of mercury during its electrodeposition from Hg$_2^{2+}$ solution. In spite of their more negative standard reduction potential, $E^{0}_{\text{Hg(II)/Hg}} - E^{0}_{\text{Hg}_2^{2+/Hg}} = -58$ mV, reduction of Hg$_2^{2+}$ readily occurs at the overpotentials required for mercury nucleation. Furthermore, by virtue of reactions (4) and (7) occurring at the surface of the growing mercury droplets and their small size during the early stages of electrodeposition, consequently enhancing their transport to the solution, the concentration of Hg$_2^{2+}$ at the electrode interface becomes comparable to that of Hg$_2^{2+}$, contributing to the supersaturation and increasing the number density of nuclei and, along with it, the effects of nucleation inhibition in their vicinity. Enhanced spatial ordering would then arise from the higher number density of nuclei on the surface during electrodeposition from Hg$_2^{2+}$ solution, due to formation of Hg$_2^{2+}$.

4. Conclusions

The kinetic studies presented in this paper show that mercury deposition from Hg$_2^{2+}$ solution occurs as a simple electrochemical reaction. In contrast, mercury deposition from Hg$_2^{2+}$ solutions occurs with low faradaic efficiencies due to the formation of Hg$_3^{2+}$, either as the reduction intermediate, through chemical disproportionation [24–28], or following both mechanisms simultaneously. In spite of these complications, it has been shown that the overpotential-dependence of the rate of Hg nucleation, when deposited from either Hg$_2^{2+}$ or Hg$_2^{2+}$ solutions, follows the predictions of the classical theory of nucleation [17,21], with a 4-fold decrease in the slope of the ln ($\theta$) versus $1/\eta^2$ plot when deposition is carried out from Hg$_2^{2+}$ as compared to Hg$_2^{2+}$ solutions. Furthermore, analysis of the kinetics of Hg nucleation under the framework of the atomistic theory [31,36,37] yielded critical nuclei with similar sizes during deposition from both Hg$_2^{2+}$ and Hg$_2^{2+}$ solutions throughout the overpotential ranges explored, as expected from the identical interactions between atoms of the deposit and the substrate in both processes. High dispersion of the data obtained for mercury nucleation from Hg$_2^{2+}$ solution at low overpotentials precluded analysis of kinetic data under such conditions. At high overpotentials, $-\eta = 0.25$ V, however, and in spite of the higher nucleation rates obtained during deposition from Hg$_2^{2+}$ solution, it was found that mercury nucleation from either Hg$_2^{2+}$ or Hg$_2^{2+}$ solutions occurred, at a given overpotential, onto a comparable number density of sites. Given the large differences between the electrochemical processes leading to Hg nucleation from Hg$_2^{2+}$ and Hg$_2^{2+}$ solutions, the similar critical nuclei sizes and number densities of sites obtained during deposition from both solutions indicate the dominant role of the deposit–substrate interactions in controlling the rate of the nucleation process.

Comparison of the saturation number densities of nuclei deduced from analysis of current transients with those obtained from the microscopic examination of the electrode surface, under the simplifying assumption of a model considering exclusion zones, indicated that the description of nucleation inhibition in the vicinity of growing nuclei needs a more representative treatment, considering the detailed distribution of stationary nucleation rates around nuclei [33].

![Fig. 12. Ratio of the standard deviation of the distances between nearest neighbours and their mean distance, $\sigma/\langle r \rangle$, for mercury nuclei deposited from 0.01 mol dm$^{-3}$ Hg$_2^{2+}$ (○) and Hg$_2^{2+}$ (△) solutions at different overpotentials. Also indicated are the $\sigma/\langle r \rangle$ values corresponding to the uniform distribution (a), and those arising from exclusion (b) and inhibition (c) of nucleation around growing nuclei (see text for details).](image-url)
At a given overpotential, the microscopically observed saturation number densities of nuclei were higher after deposition from \( \text{Hg}^2+ \) compared with \( \text{Hg}^2+ \) solution. Even though the critical nucleus size and the number density of sites on the surface do not depend on the oxidation state of the electrodepositing species, the nucleation rate depends strongly on the number of electrons transferred during the process, cf. Eq. (3), thus leading to higher nuclear number densities. At low overpotentials, the nuclei deposited from either solution were uniformly distributed on the electrode surface, whereas their distribution was affected by inhibition of the nucleation rate close to already established nuclei at higher overpotentials.

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References