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Analysis of the differential capacity at the silver/lithium perchlorate aqueous solution interface

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Abstract Analysis of the differential capacity of ideally polarized Ag electrodes without specific adsorption is presented. The capacity was measured for three crystal faces of Ag [(111), (100) and (110)] and for polycrystalline Ag in aqueous solutions at different concentrations of LiClO₄. The inner layer contribution C_i was analysed for all the systems studied according to Grahame's concept. Moreover, using the procedure proposed by Amokrane and Badiali, several contributions to C_i , i.e. the metal (C_m), the solvent (C_s) and dipole orientation (C_{dip}), were calculated. The influence of the kind of crystal face of the Ag electrode on the values of these contributions is discussed.

Key words Crystal silver electrodes · Differential capacity · Silver/electrolyte interface

Introduction

In electrosorption studies of organic substances on solid electrode surfaces (particularly in the case of Ag or Au electrodes), the LiClO₄ electrolyte was often used as a supporting electrolyte since it is not specifically adsorbed on these metals. It seemed to us that it would be advantageous to collect more information about the properties of these interfaces without any organic adsorbate on the electrode. Various models have been proposed in the literature [1–4] for interpretation of experimental capacity curves. In most classical models the emphasis is put on the orientation, in the electrical field, of the solvent dipoles in the layer adjacent to the

metal surface [1]. A common point to all classical models is that the metal, considered as a perfect conductor, does not contribute directly to the capacity. Its effect is, however, incorporated in the models by considering a specific interaction of a chemical nature between the solvent and the metal. A direct contribution of the metal has been considered in the models presented during the early 1980s [3, 4].

According to Amokrane et al. [5–7], the contribution of the metal denoted as C_m is expressed by the term $X_0(\sigma)$ of Eq. 17 in [5], i.e. by relaxation of the surface dipole of the metal with the charge and also by the value of the metal-solvent distance, d , and its variation with the charge of the electrode. Hence, one of the major aspects introduced by the recent models [2–7] is that the potential drop of the metal changes with the charge. In effect, C_m contributes to the inner layer capacity C_i , in contrast to the classical models where $C_m^{-1} = 0$. Amokrane et al. [5] described a method of determination of C_m values and reported the corresponding data for the Ag(111) electrode. Knowing C_m and C_i from experimental data, one may calculate the contribution of the solvent using the relation [5]:

$$C_s^{-1} = C_i^{-1} - C_m^{-1} \quad (1)$$

Amokrane et al. [5] applied this method to the experimental data obtained by Valette et al. [8] for Ag(111) in NaF and by Valette [9] for Ag(110) and (100) in aqueous solutions of KPF₆. It should be born in mind, however, that whereas PF₆⁻ ions do not adsorb on a silver electrode, this is not the case for F⁻ ions [9]. The authors [5] suggested that although some differences could be observed in the curves of C_s versus σ (where σ is surface charge density) for the three low-index faces of silver around the maximum of C_s , it was not possible to discriminate significantly between these three faces. In our opinion, however, it is difficult to compare the data obtained in solutions of various anions (F⁻ and PF₆⁻) which have opposite effects on the water structure. Therefore, in this paper we consider the behaviour of C_i ,

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C_m and C_s with the charge on three Ag crystal faces [(110), (100) and (111)] and on the polycrystalline Ag electrode in solutions containing LiClO_4 (ClO_4^- anions practically do not adsorb on Ag). Since in the measurements reported in this paper we used a supporting electrolyte other than those used by Amokrane et al., additionally we are able to estimate the specific effect of different ions on the capacity contributions. For various alcohols which have been studied by us previously [10], the effect of the electrolyte nature was clearly observed.

Experimental

Solutions

LiClO_4 (Merck) was recrystallized twice from triple-distilled water. All the solutions were prepared using distilled and deionized water (from Q-Millipore) with a resistivity of 18 $\text{M}\Omega$ cm. The solutions were deaerated with purified argon. All experiments were carried out at 23 ± 1 °C.

Electrode and experimental technique

Experiments were carried out in a standard electrochemical cell with three electrodes. The counter electrode was a platinum sheet placed parallel to the working electrode surface, while a saturated calomel electrode (SCE) was the reference electrode. The working electrodes were cylindrical silver crystals [(110), (100) and (111)] oriented by X-rays. Mechanical polishing and then chemical cleaning in a bath based on CrO_3 , according to [11], were performed before each experiment. After polishing, the electrode was soaked in concentrated perchloric acid for about 5 min and then rinsed with distilled water in an ultrasonic bath.

The quality of the silver electrodes prepared in this way was verified by cyclic voltammetry. Electrochemical and admittance measurements were performed using AUTOLAB with GPES and FRA modules (Eco Chemie, Netherlands). The plots of the complex plane $Z'-Z''$, where Z' is a real and Z'' is imaginary part of the impedance (or $Y'-Y''$ where Y' is a real and Y'' is imaginary part of the admittance) diagrams [12] were collected at each potential (ranging from -1.2 V to -0.2 V) in steps of 50 mV in the frequency range between 10 Hz and 200 Hz. In order to check whether the capacity obtained is the equilibrium value, the electrode impedance was studied as a function of frequency. The equilibrium capacity C (zero frequency capacity) was obtained from the intercept of the $C = f(\omega^{1/2})$ dependence at $\omega = 0$ (where ω is the angular frequency).

A roughness factor R of the silver electrodes, derived from a Parsons-Zobel graph [13], was 1.15 for Ag(110), 1.01 for Ag(100), 1.09 for Ag(111) and 1.15 for polycrystalline Ag. All zero frequency capacities were divided by product sR , where s is the geometrical area of the electrode, and then presented on the figures.

Results and discussion

Differential capacity curves

Differential double-layer capacity versus potential curves, C vs. E , for the three faces of the Ag electrodes and also for the polycrystalline electrode were measured for several concentrations of LiClO_4 , ranging from 0.003 to 0.1 mol dm^{-3} . The C vs. E curves are shown in

Figs. 1–4. The diffuse-layer minima are visible for all crystal faces for all concentrations of LiClO_4 even as high as 0.1 mol dm^{-3} . This means that $C_i > C_d$ (where C_d is the capacity of the diffuse layer calculated using the Gouy-Chapman theory). Hence, if diffuse minimum appears in C vs. E curves for higher concentrations of electrolyte ($c > 0.01$ mol dm^{-3}), one may expect that the values of C_i for this interface are much higher than those for the mercury/solution interface. Independence of the position of this capacity minimum of LiClO_4 concentration, with an accuracy of ± 5 mV, may indicate the lack or very weak specific adsorption of anions. In this case, E_{min} may be identifiable with the potential of zero charge (pzc), being equal to -0.950 ± 0.005 V for polycrystalline Ag, -0.975 V for Ag(110), -0.865 V for Ag(100) and -0.695 V for Ag(111). In consequence, the differential capacity versus potential curves follow the model of the double layer in the absence of specific adsorption expressed by the well-known equation:

$$C^{-1} = C_i^{-1} + C_d^{-1} \quad (2)$$

C_i curves

In the absence of specific adsorption, the extrapolation of the C^{-1} vs. C_d^{-1} plot to the infinite large concentration at the pzc gives the value of C_i . According to Grahame's

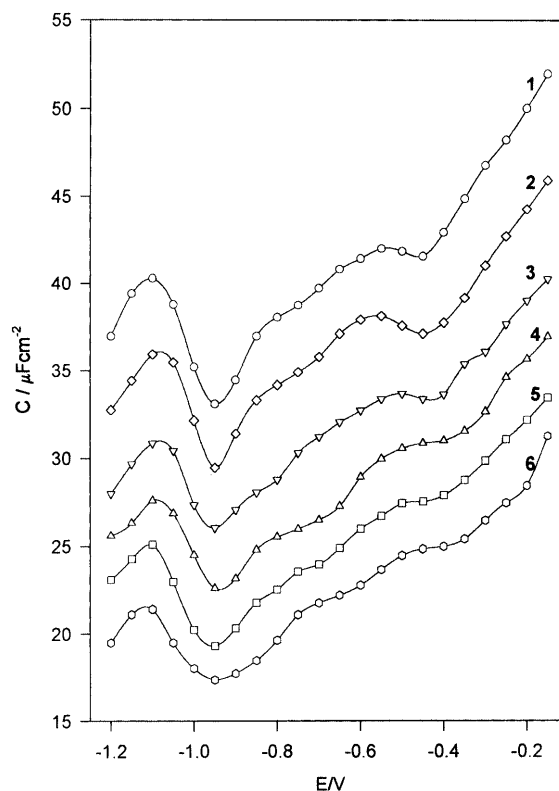


Fig. 1 Differential capacity vs. potentials curves for a polycrystalline Ag electrode in solutions containing different concentrations of LiClO_4 (mol dm^{-3}): 0.1 (1); 0.05 (2); 0.03 (3); 0.02 (4); 0.01 (5); and 0.0075 (6)

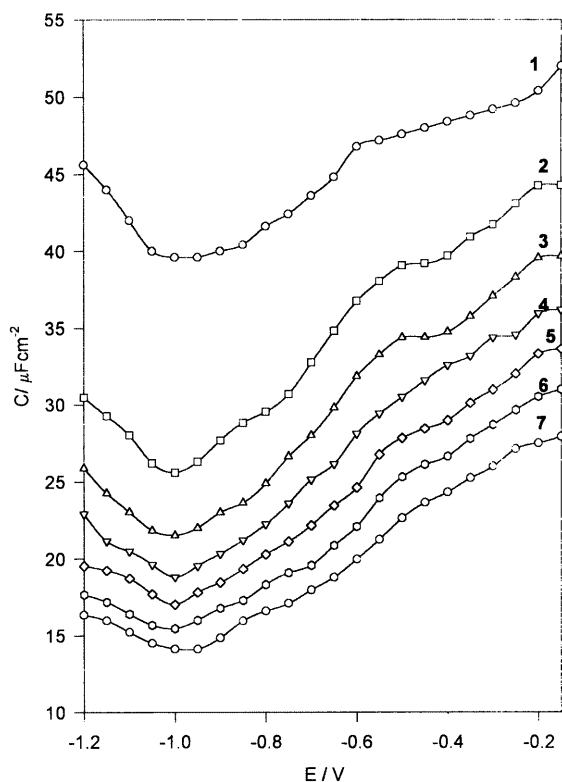


Fig. 2 Differential capacity vs. potentials curves for an Ag(110) electrode in solutions containing different concentrations of LiClO_4 (mol dm^{-3}): 0.1 (1); 0.05 (2); 0.03 (3); 0.02 (4); 0.01 (5); 0.0075 (6); and 0.003 (7)

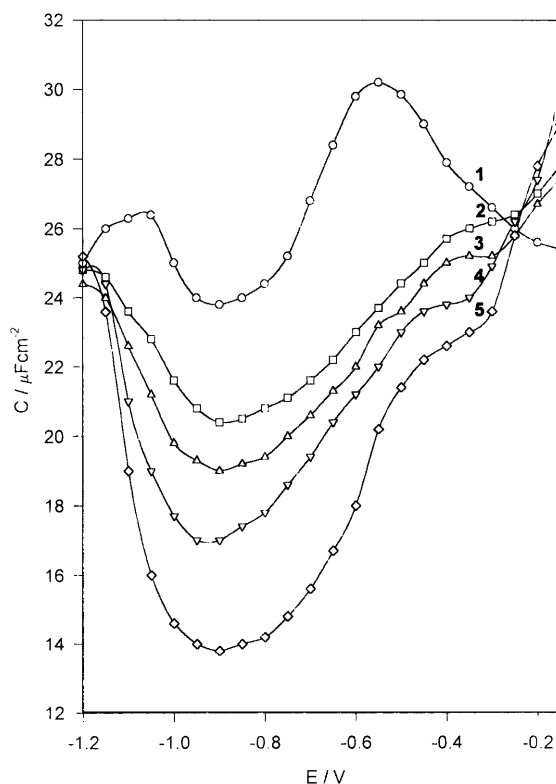


Fig. 3 Differential capacity vs. potential curves for an Ag(100) electrode in solutions containing different concentrations of LiClO_4 (mol dm^{-3}): 0.1 (1); 0.05 (2); 0.03 (3); 0.02 (4); and 0.01 (5)

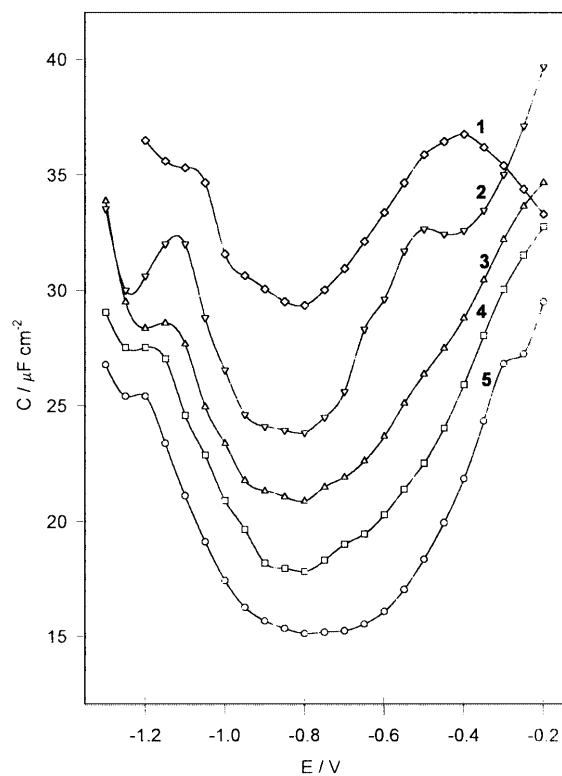


Fig. 4 Differential capacity vs. potential curves for an Ag(111) electrode in solutions containing different concentrations of LiClO_4 (mol dm^{-3}): 0.1 (1); 0.05 (2); 0.03 (3); 0.02 (4); and 0.01 (5)

idea, the inner layer is filled only by the water molecules [14]. The values of C_i obtained for all Ag electrodes studied, summarized in Table 1, are smaller than that obtained by Valette [9] for KPF_6 solutions, but the sequence of C_i is the same for both electrolytes. It seems to us that the kind of supporting electrolyte may influence the arrangement of the water molecules in the inner layer.

The dependence of C_i on the charge of the electrode for all Ag electrodes studied in solutions of $0.01 \text{ mol dm}^{-3} \text{ LiClO}_4$ and $0.1 \text{ mol dm}^{-3} \text{ LiClO}_4$ is shown in Figs. 5 and 6, respectively. As can be seen, both parameters, i.e. the crystal face of Ag and the electrolyte concentration, affect the shape of C_i vs. σ curves and the magnitude of C_i . The increase of electrolyte concentration results in an increase of the height of peak C_i without changing its position on the potential scale.

Table 1 The capacity contributions to the Ag/ LiClO_4 solution interface ($\mu\text{F cm}^{-2}$)

Ag	C_i^a (at $\sigma_m = 0$)	$-C_m$ (at σ_{\max})	C_s (at σ_{\max})
Poly	85	98	53
110	70	80	66
100	42	222	37
111	40	345	36

^a From extrapolation of $1/C$ vs. $1/C_d$ to $(1/C_d) \rightarrow 0$

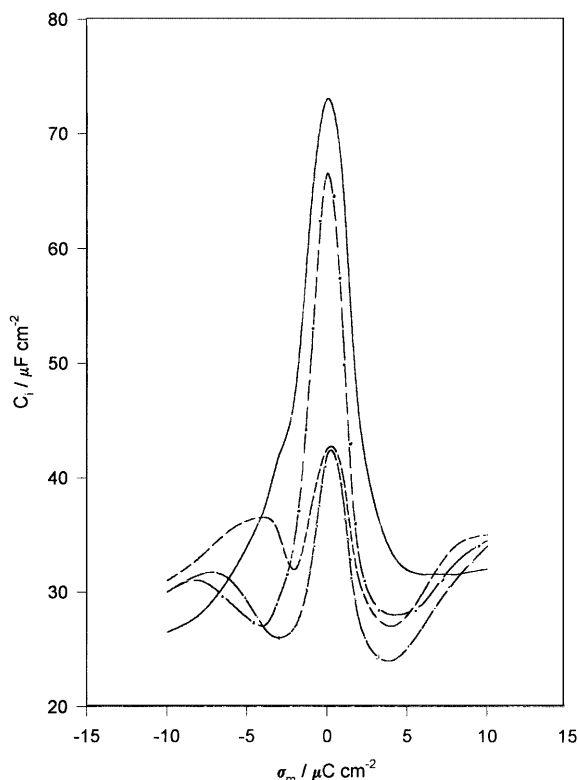


Fig. 5 Variation of C_i with charge in solutions of 0.01 mol dm^{-3} LiClO_4 for different electrodes: (—) polycrystalline Ag; (· · ·) Ag(110); (---) Ag(100); and (—×—) Ag(111)

Grahame [14] assumed that the inner layer capacity C_i , for the case when the diffuse minimum in the capacity curves (C vs. E) disappears, depends only on the charge of the electrode and then usually the maximum of C_i in the C_i vs. σ curves is not observed. However, this is not the case for the systems studied by us except Ag(111)/ 0.1 mol dm^{-3} . For that interface the C_i maximum is practically not observed (Fig. 6), which suggests that the diffusion effect is markedly smaller than that for other Ag systems.

Moreover, the shapes of the C_i vs. σ curves observed in Fig. 6 may testify that the structures of the inner layer at the silver electrodes (110) or (100) are different from those at Ag(111) or Hg. This may be caused by a different arrangement of the metal atoms at the electrode surface, leading to various electronic interactions between the metal atoms and ions at the interface. On the other hand, these interactions may be also dependent on the distribution of the water molecules in the inner layer, which is different for various crystal faces of Ag.

In general, specific adsorption of ions facilitates the disappearance of the diffuse minimum in the C vs. E curve (the minimum disappears even at low ion concentrations in the solution). The minima, which are visible in the C vs. E curves [except Ag(111)/ 0.1 mol dm^{-3} LiClO_4 system] in Figs. 5 and 6, may suggest that the specific adsorption of ClO_4^- is rather negligible. Moreover, since in our studies the values of

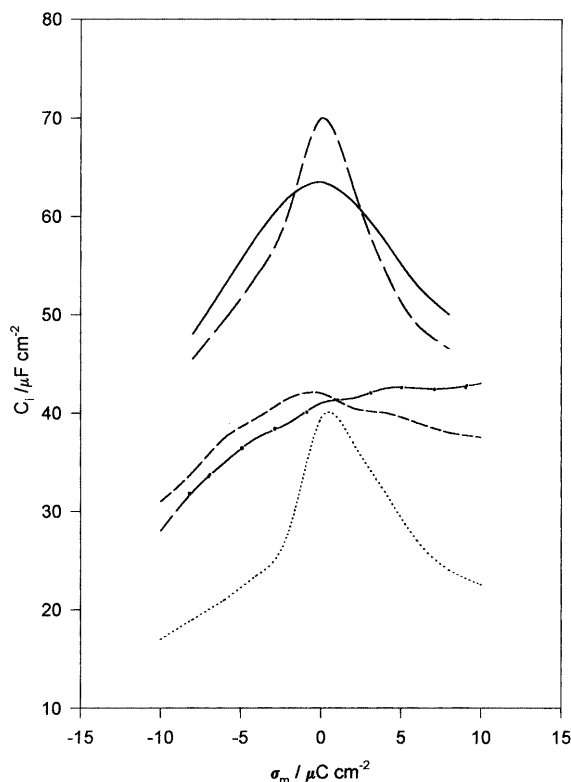


Fig. 6 Variation of C_i with charge for different electrodes: (—) polycrystalline Ag; (— —) Ag(110); (· · ·) Ag(100); and (- · -) Ag(111) in solutions of 0.1 mol dm^{-3} LiClO_4 , and (· · ·) for the Hg/ KPF_6 solution interface

C_i depend on the ion concentration, the effect of the diffuse-layer contribution likely dominates the total C values in the range of concentration studied. The comparison of the courses of the C_i vs. σ curves, presented in Fig. 6, may suggest very similar electrical behaviour of the polycrystalline and Ag(110) electrodes (having more complex surface atomic distribution). The similarity is also visible in the behaviour of Ag(100) and Ag(111) electrodes having smoother surfaces.

Analysis of C_i

According to the classical model [14], Valette [15] used the values of C_i at the pzc to determine the silver-water interactions. Moreover, Valette observed that in KPF_6 solutions the values of C_i do not change with ion concentration at far negative potentials, being almost equal to $K_{\text{ion}} \equiv \epsilon/(4\pi r)$ (where ϵ is the electric permittivity in the inner layer and r is the molecular diameter of the solvent molecules). Thus, the K_{ion} value may correspond to the capacity of a monolayer of water dipoles oriented with their negative ends towards the solution [16, 17]. However, for different electrodes the corresponding values of C_i change at far negative polarization potentials from about $16 \mu\text{F cm}^{-2}$ for Hg [14] to $25 \pm 1 \mu\text{F cm}^{-2}$ for Ag(110) and to $20 \pm 1 \mu\text{F cm}^{-2}$ for Ag(111) [9]. Thus, according to the classical model,

the variations of K_{ion} may be mainly ascribed to the changes of the inner layer thickness (this thickness is greater for the Hg electrode than for the Ag electrode). In contrast to the classical model, the recent models of a double layer [5] also introduce into C_i a contribution of the metal, C_m (cf. Eq. 1). Amokrane and Badiali [6] described the metal by a jellium-like model. The authors included three terms into the equation for C_m^{-1} (Eq. 17 in [5]). As well as the value of the metal-solvent molecules distance d and its variation with the charge $\sigma(\partial d/\partial\sigma)$, a third term reflects the relaxation with charge of the surface dipole of the metal $X_0(\sigma)$. Taking into account these effects, Amokrane et al. [5] have calculated C_m values for Ag(111). By using them to compare the capacitance behaviour of different crystal faces of Ag in interfaces in the same solution ($0.1 \text{ mol dm}^{-3} \text{ LiClO}_4$ aqueous solution), Eq. 1 can be used essentially in two different ways.

Firstly, one may assume that C_s is a “universal” quantity in a given group of Ag electrodes. Then, taking corresponding data for Ag(111), i.e. experimental C_i values and C_m obtained from [6], one attains the related C_s using Eq. 1. Then C_s values can be used in conjunction with different experimental C_i data for other Ag electrodes, to obtain the corresponding C_m values.

The second way is exactly the converse of the first method. Now it is assumed that C_m is a “universal” quantity in that Ag group. Further, the C_m values for Ag(111) (taken from [6]) are used for other Ag electrodes to calculate C_s using the experimental data for C_i (for each electrode studied). In next section we will examine our systems by both methods.

The first approach (C_s is constant)

C_m vs. σ and C_m^{-1} vs. σ curves determined by means of the first method (assuming C_s as a “universal” factor) are shown in Figs. 7 and 8, respectively. The C_m vs. σ curves for different monocrystalline Ag electrodes are quantitatively different, particularly in the vicinity of the pzc, but the extrema of all curves are located at the same charge density σ (Fig. 7). Moreover, at positive charges the C_m vs. σ curves practically converge, whereas at negative charges the curves only approach the same value. However, the differences between the C_m vs. σ curves for various crystal faces of Ag are easier to explain by analysis of C_m^{-1} vs. σ dependence, presented in Fig. 8.

According to discussion of the Eq. 17 in [5], C_m^{-1} is affected mainly by the value of d , i.e. by the distance of the closest approach of the solvent molecules to the metal surface and by the term $\sigma(\partial d/\partial\sigma)$. As visible in Fig. 8, the curves of C_m^{-1} vs. σ are bellshaped with a maximum at a small negative charge density ($\sigma_m = -2 \mu\text{C cm}^{-2}$ for all monocrystalline and $-1 \mu\text{C cm}^{-2}$ for polycrystalline electrodes). According to Amokrane et al.'s model [5], the position of the maximum for $1/C_m$

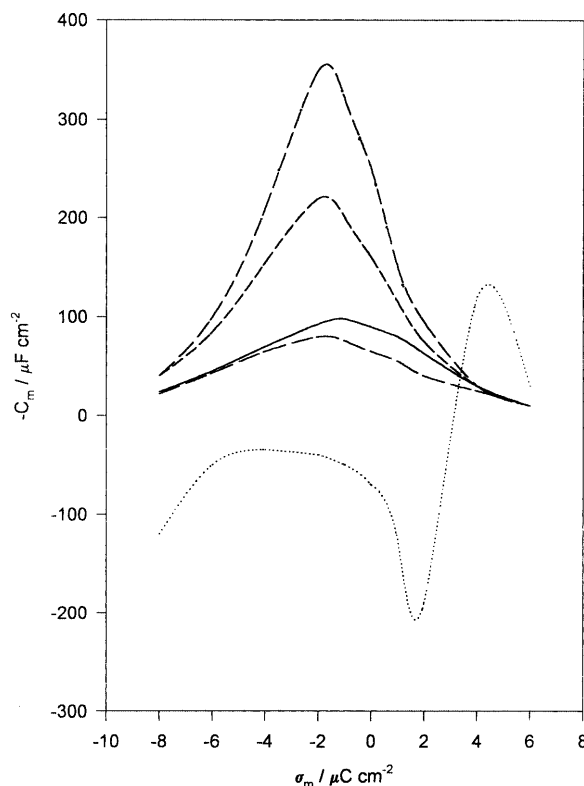


Fig. 7 Variation of $-C_m$ with charge for (from top to bottom) Ag(111)/NaF (—) (from [6]) and for Ag(100), polycrystalline Ag, and Ag(110) in solutions of $0.1 \text{ mol dm}^{-3} \text{ LiClO}_4$, and for the Hg/NaF interface (· · ·) (from [7])

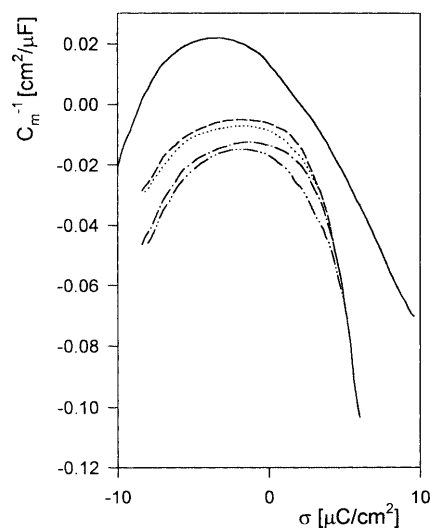


Fig. 8 Variation of C_m^{-1} with charge for (from top to bottom) the Hg/NaF interface (—) (from [7]), for Ag(111)/NaF (---) (from [6]) and for Ag(100), Ag(poly) and Ag(110) in solutions of $0.1 \text{ mol dm}^{-3} \text{ LiClO}_4$

at σ_m is close to the maximum of d in the curve of d vs. σ . Hence, the σ_m values obtained indicate the maximum of d in the system studied. The values of $1/C_m$ for different Ag crystal faces may be ordered in the following

sequence: Ag(111) > Ag(100) > Ag(poly) > Ag(110). The differences observed may arise from various reasons: differences in the electron densities or changes of the effective distance d of the solvent molecules from the surface. These effects may be strongly dependent on the arrangement of the metal atoms on the electrode surface. Probably, in our studies the second effect is significant [d increases on passing from Ag(110) to Ag(111)].

The second approach (C_m is constant)

Using the C_m results for Ag(111) (from [6]) and the values of C_i obtained experimentally, we calculated the values of C_s for the Ag electrodes studied. The C_s vs. σ curves, shown in Fig. 9, differ qualitatively from the C_i vs. σ curves presented in Fig. 6. At extreme negative charges, C_s is always smaller than C_i . It is clear that the behaviour of C_s is dictated by the behavior of C_m (C_m and C_s are of comparable magnitude except the sign, but not equal). The C_s vs. σ curves have a bell shape, almost symmetrical with respect to the position of a maximum, which appears for all Ag electrodes at $\sigma_{\max} = -1 \mu\text{C cm}^{-2}$, as for Hg/KPF₆ solutions (the C_s vs. σ curve for Hg was obtained from data presented by Baugh and Parsons [18]). On the other hand, for the Hg/NaF solution interface, the value of σ_{\max} was about

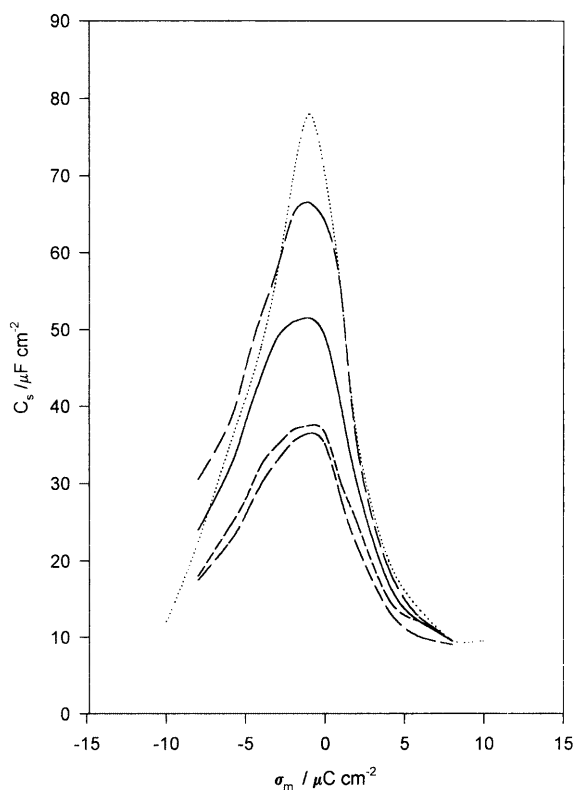


Fig. 9 Variation of C_s with charge for (from top to bottom) the Hg/KPF₆ solution interface calculated using the data from [18] and for Ag(110), polycrystalline Ag, Ag(100) and Ag(111) in solutions of $0.1 \text{ mol dm}^{-3} \text{ LiClO}_4$

$-2 \mu\text{C cm}^{-2}$ [7], being identical with that for the Ag(111)/NaF system [6]. These results indicate that the nature of the supporting electrolyte influences the water structure in the inner layer. The value of σ_{\max} is related to the orientation of the solvent dipoles in the field generated both by the effective charge on the electrode and by the dipoles themselves. The negative sign of σ_{\max} means that the water molecules are oriented at the pzc with the negative end of the dipole towards the electrode.

C_s or C_m as a “universal quantity”

The assumption of “constant C_s ” is, in our opinion, more plausible. The difference between the courses of the C_m vs. E curves for different metals can then be rationalized, in the case when the solution adjacent to the electrode is always the same. Then, if the differences in the experimental curves are attributed to the differences in the contributions of the metals, the C_s vs. σ curves should be identical and should mainly reflect the orientation of the solvent dipoles in the external electrical field.

Under the assumption of constant C_m it was observed that the C_s vs. σ curves in all cases are symmetrical with respect to the position of the maximum at a negative charge σ_{\max} , which is the same for all electrodes. Thus, this fact indicates the same orientation of the water dipoles adjacent to the electrode in all systems studied. However, the $C_s(\max)$ values should be the same in the same solutions, but this is not the case. Thus, the different values of $C_s(\max)$ observed in Fig. 9 may result from the fact that the crystal face Ag electrode effects were not taken into account under assumption of constant C_m .

C_{dip} curves

The dipolar contribution C_{dip} , associated with the orientation of the permanent dipoles, was found by applying the equation [7]:

$$1/C_{\text{dip}} = 8\pi R_0/\varepsilon - 1/C_s \quad (3)$$

We assumed that the thickness of the water monolayer at the electrode $R_0 = 0.3 \text{ nm}$, and that $\varepsilon = 2$ since this value corresponds to the high-frequency limit of the electric permittivity. The C_{dip} vs. σ dependence for various Ag electrodes is shown in Fig. 10. The results give evidence for a lack of influence of the kind of metal on C_{dip} values for the same solution except for far positive charges, where small differences are visible. C_{dip} values reflect competition between the orienting effect imposed by the external field on the solvent dipoles and the effect of dipole-dipole interactions. The former effect can be expressed by the factor $f(\xi) = \partial \langle \cos\theta \rangle / \partial \xi$ (where θ is the angle between the dipole and the normal to the electrode

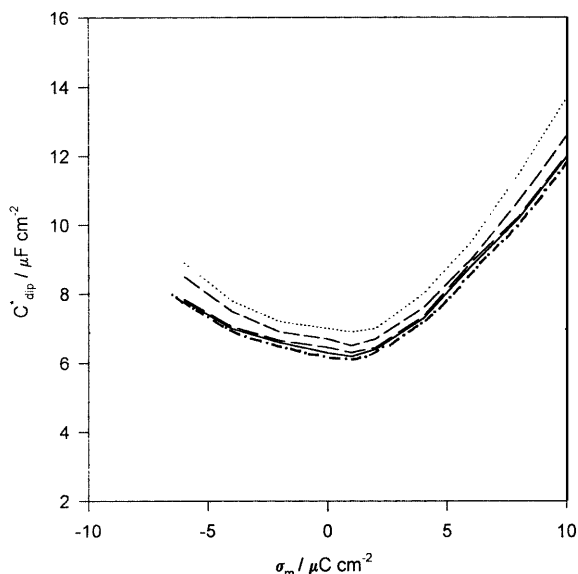


Fig. 10 Variation of C_{dip}^* (for effective charge $\sigma^* = \sigma - \sigma_{\text{max}}$) with (from top to bottom) the charge for Ag electrodes (100), (111), (110) and polycrystalline Ag for the Hg/KPF₆ solution interface corresponding to the C_s values from Fig. 9

surface), which defines the rate of change of the average dipole orientation [7]. Following the arguments of Amokrane and Badiali [7], C_{dip} is inversely proportional to $f(\xi)$. Thus, interpreting the resulting curves C_{dip} vs. σ (Fig. 10) for moderate charges of the electrode, one may assume that the rate of change of the average dipole orientation with the charge is practically independent of the crystal face of Ag and also of the kind of metal. It should be noted, however, that for far positive charges the values of C_{dip} for Ag(100) and Ag(111) are slightly higher than those for Ag(110) and for the polycrystalline

electrode. This may indicate that, in this case, the rate of the change of the average dipole water orientation under an external electric field is higher in the case of Ag(110) and the polycrystalline electrode than for Ag(100) or Ag(111).

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