

On the Differential Capacitance and Potential of Zero Charge of Au(111) in Some Aprotic Solvents

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Voltammetric and Gouy-Chapman capacitance minimum measurements were conducted on Au(111) and roughened Au(111) electrodes in aprotic electrolytes in the absence and presence of specifically adsorbed ions for concentrations ranging from 0.001 to 0.5 M. Negative of the point of zero charge (pzc), the capacitance maximum increases in the order $\text{Ca}^{2+} < \text{Li}^+ < \text{K}^+$, but the pzc value is independent of cation nature. The capacitance values have a slight dependence on cation type at a more negative potential. The pzc depends on the solvent and is influenced by the dielectric constant, metal-solvent interactions and donor number; it is shifted to more positive values with increasing water content. Specific anion adsorption shifts the pzc to more negative values. The pzc value is more negative

for the roughened electrode compared to the single crystal electrode. Propylene carbonate (PC) adsorption in the presence of perchlorate and iodide was examined on gold film by surface-enhanced infrared absorption spectroscopy (SEIRAS). The potential dependent intensity is explained by a stronger electric field and thus a better alignment of the PC molecules when the absolute potential difference to the pzc is large. The capacitance curves were theoretically modelled. From the capacitance maxima on both sides of the pzc the ionic volume and thus the solvation numbers were estimated. The width of the capacitance minimum is believed to be related to the layer of adsorbed solvent molecules.

1. Introduction

Within the framework of recent research for better energy storage systems like batteries, and fuel cells based on non-aqueous electrolytes with their wider potential range are becoming more and more important. A deeper understanding of the electrochemical interface is a requirement for further development of these systems and the underlying processes. The properties of electrode/ electrolyte interface structure are influenced by some factors such as kind and concentration of ions,^[1,2] nature of solvent molecules, and atomic structure of the electrode.^[3] For instance, different cations can result in a redistribution of the potential drop in the interfacial double layer and improvement of the anion adsorption rate.^[4,5] Besides variation of organic solvents affects the intensity of double-layer capacitance through differences in electrolyte resistance

and relaxation time constant of an electrical double layer (EDL).^[6,7]

The potential of zero charge (pzc) is of fundamental significance in surface electrochemistry and its importance lies in providing information about the structure of the electrode/ electrolyte interface. Several techniques are available for the determination of the pzc. One of these consists in measurements of capacitance curves and location of the capacitance minimum caused by the diffuse double layer contribution to the total differential capacitance in dilute solutions (according to the Gouy-Chapman-Stern model). The correlation with the electronic work function of the electrode is clearly established.^[8,9] Frumkin and Petri have proposed two different pzcs to determine the fundamental magnitudes of Pt/ electrolyte interface and are potential of zero total charge (pztc) and potential of zero free charge (pzfc).^[10] The pztc has been observed and measured due to transferring the total charge involving the transferred charge during the chemisorption of e.g. hydrogen atoms. While the pzfc (electronic charge lying on the electrode) is observed in absence of adsorption of species and is equivalent to pzc for simplicity.^[11]

There is a wealth of capacitance data for single crystal electrodes in aqueous electrolytes such Au (111),^[12–17] Ag (111)^[12,18–22] and other single crystals^[1,23–25] in addition to measurements of the pzc with the immersion technique.^[26] Opposed to that, measurements of the pzc of the Au(111) or other single crystal surfaces in aprotic electrolytes in absence and presence of specific adsorption have hardly been reported except for very few studies, e.g. in PC on polycrystalline Au and DMSO on single crystalline Au.^[27–29] In ionic liquids, the pzc of Au(111) and Au(100) was determined using the immersion technique.^[30,31]

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The pzc has been determined in organic solvents on polycrystalline electrodes such as Au electrode,^[32–34] silver electrode,^[11,35] and platinum electrode.^[36] In addition many studies have been reported for mercury,^[37–44] gallium and indium-gallium alloys,^[45–54] bismuth.^[47,55,56]

Experimental capacity curves can be analyzed with a continuum thermodynamic modeling framework, which is capable of predicting qualitatively and quantitatively the charge and capacity of the double layer.^[57] In section 3 we briefly review some modeling aspects, most importantly how internal pressure and incompressibility of the solution are coupled through the partial molar volume of the solvated ions. It is shown that the thermodynamic consistent modeling of this effects yields a saturation in the space charge layer, which proves as the origin of the double layer capacity maxima and entirely neglected in the Gouy-Chapman theory.^[58,59] The scaling parameter for the capacity maxima is the partial molar volume of the solvated cation (negative of the pzc) and the anion (positive of the pzc), which allows us to deduce actual values from experimental data. Due to solvation effects, the partial molar volume of anions and cations is related to their respective solvation number,^[58,59] which can thus be deduced from capacity measurements. Further we briefly address the question how the charge number influences the partial molar volume of solvated cations in section 4.3.

In situ SERS together with capacitance-potential curves were used to estimate the pzc on polycrystalline Ag electrode in a Br[−] containing DMSO electrolyte.^[27] Recently the influence of cations of perchlorate salts on adsorption of acetonitrile on gold film was investigated by using SEIRAS.^[60]

The properties of the electrical double layer in various ionic liquid on many polycrystalline and single crystal electrodes were reviewed in detail.^[61] In situ surface-enhanced Raman spectroscopy connected with differential capacitance measurements was established to estimate the pzc values for several ionic liquids on the silver electrode.^[62] It has been determined for a variety of ionic liquids by using capacitance-potential measurements on Au, Hg, Gc, and Pt electrodes.^[63,64]

The goal of this study is to elucidate the influence of the solvent properties on the position of the pzc of a well-oriented Au(111) and a roughened electrode. Also, the influence of the water content, and cation and anion identity on the point of zero charge of the Au (111) electrode will be studied. We furthermore characterize the interface using SEIRAS. This is a continuation of our efforts to elucidate the influence of the solvent on the extent and rate of ionic adsorption. A more general aim of this paper is to elucidate whether and to demonstrate that, such surface-sensitive measurements are possible at single crystals in aprotic solvents.

Experimental Section

Chemicals and Materials

Potassium perchlorate (KClO₄, ≥ 99%, SIGMA-ALDRICH), potassium hexafluorophosphate (KPF₆, ≥ 99%, ACROS), (KBr, ≥ 99.5%, MERCK),

lithium perchlorate (LiClO₄, ≥ 99%, SIGMA-ALDRICH), calcium perchlorate tetrahydrate (99%, Sigma Aldrich) was dried under reduced pressure and T = 83 °C in a Büchi-oven for 48 h prior to further use), silver nitrate (AgNO₃, ≥ 99%, SIGMA-ALDRICH), decamethylferrocene (Me₁₀Fc, 97%, SIGMA-ALDRICH), H₂SO₄ spectra pure grade (Merck), propylene carbonate (PC, 99.7%, SIGMA-ALDRICH) and acetonitrile (ACN, 99.8%, ACROS), Diethylene glycol dimethyl ether (Diglyme, DG, 99.5%, anhydrous, dried over a molecular sieve), Dimethyl sulfoxide (DMSO, 99.7%, over molecular sieve) were used. All aqueous cleaning solutions were made with 18.2 MΩ cm Milli-Q Millipore water. The electrolytes have been deaerated with very pure argon (99.999%, AIR LIQUIDE).

Glasses, Teflon, and PCTFE materials have been treated with 5 M KOH solution to remove organic pollutants, as well as inorganic contaminants are eliminated by immersion into chromic acid.

Electrochemical Conditions and Instrumentation

All tests were conducted at room temperature in a three-compartment electrochemical cell. The working electrode was a gold single crystal disk electrode (Au(111)) (φ = 10 mm) and was electrochemically cleaned by cycling in 0.1 M sulfuric acid solution in the potential range between 0.03 to 1.8 V vs. RHE. It was annealed by gas flame and cooled in an inert gas (Ar), as described previously.^[5] The accuracy of the preparation was examined by cyclic voltammetry between 0.03 and 1.2 V in hanging meniscus configuration in 0.1 M H₂SO₄. An Au sheet acted as the counter electrode for cyclic voltammetry and differential capacitance measurements. For the measurements in the non-aqueous electrolytes, the Au(111) electrode was quickly cooled down in an Argon stream, and then rapidly was moved to the cell, which set for non-aqueous electrolytes. In the supporting information (Figure S1) we show by cyclic voltammetry in sulfuric acid that the Au(111) electrode stays clean and well-ordered after the measurement in the organic electrolyte.

The water content was determined by Karl Fischer titration and was approximately 35 ppm in PC, 31 ppm in DMSO, 20 ppm in ACN, and 45 ppm in DG after the electrochemical experiments.

Potentials were recorded versus an Ag | Ag⁺ reference electrode in either DMSO or ACN containing 0.1 M AgNO₃ depending on the type of electrolyte in the working electrode compartment connected to the cell by a Luggin capillary. The potential scale of the reference electrode was calibrated using decamethylferrocene (DMFc) (SI Table S1) as a reference redox system, and its potential is regarded as more solvent independent than that of the Fc⁺/Fc couple.^[65] Thus we report pzc values of Au(111) electrode versus the DMFc⁺/DMFc reference system for comparability. E_{1/2} (vs. Ag/Ag⁺) for DMFc⁺/DMFc in DMSO, PC, ACN, and DG is −0.342, −0.484, −0.457, and −0.317 V, respectively. Electrode potentials were controlled with an EG&G potentiostat (model 273 A) (National Instruments GmbH, Munich, Germany). The cyclic voltammograms were recorded using LabVIEW software.

In situ FTIR spectroscopic measurements were conducted on Nicolet iS50 FTIR spectrometer fitted with a liquid nitrogen-cooled MCT-A detector in conjunction with a single-reflection mirror adapter prepared for spectrum acquisition. The incident angle of the IR beam was at 60 °. Parker Balston adsorption dryer cleaned the accessories of the optical bench and mirror attachment with dry, CO₂-free air. A 4 cm^{−1} spectral resolution, resulting in a final data spacing of 0.5 cm^{−1} was used for all measurements. The spectrum is an average of 32 interferograms. Results are shown as absorbance, log (R₀/R), where R₀ is the reference potential reflectance which is demonstrated in each measurement. As a consequence, elevated peaks signify gain or enhanced adsorption of particles, while decreased bands (downward) reflect species

reduction. The spectroelectrochemical cell used for SEIRAS measurements was previously described in detail.^[60]

Differential Capacitance Measurements and Data Analysis

The capacitance-potential curves for the Au(111) | interface were determined by measuring the in- and out - of phase components of the interfacial impedance using a Lock-in amplifier (EG&G, model 5210). At a constant frequency of 10 Hz, the real and imaginary parts of the impedance were determined, and the potential was swept with 10 mV per second from -1.0 to 0.8 V versus Ag | Ag⁺. Measured impedance values of the impedance were evaluated using the equivalent circuit shown in Figure 1. It is composed of a resistance (R_{el}), which represents the electrolyte resistance in series with a parallel combination of a capacitance (C_{DL}), which represents the double-layer capacitance, and another resistance (R_{ct}) which represents the charge transfer resistance. The time constant was set to 300 ms and the amplitude u_{ac}^0 was 3 mV.

As described before^[66,67] particularly for electrolytes with low conductivity, the superimposed AC potential has to be corrected for i_{ac} potential drop as follows:

$$u_{ac}^{corr} = u_{ac}^0 - R_{el}i_{ac} \quad (1)$$

Where, $i_{ac} = i_{ac}^r + ji_{ac}^i$

Here, i_{ac}^r and i_{ac}^i are the real and imaginary parts of the ac current, respectively. Dividing i_{ac} by u_{ac}^{corr} gives:

$$\begin{aligned} \frac{i_{ac}}{u_{ac}^{corr}} &= \frac{i_{ac}^r + ji_{ac}^i}{u_{ac}^0 - R_{el}(i_{ac}^r + ji_{ac}^i)} = \\ &= \frac{i_{ac}^r(u_{ac}^0 - i_{ac}^r R_{el})}{(u_{ac}^0)^2 - 2u_{ac}^0 R_{el}i_{ac}^r + (R_{el}i_{ac}^r)^2 + (R_{el}i_{ac}^i)^2} + \\ &+ j \frac{i_{ac}^i(u_{ac}^0 - i_{ac}^r R_{el})}{(u_{ac}^0)^2 - 2u_{ac}^0 R_{el}i_{ac}^r + (R_{el}i_{ac}^r)^2 + (R_{el}i_{ac}^i)^2} \\ &= Y_{re-corr} + jY_{im-corr} \end{aligned} \quad (2)$$

Here, $Y_{re-corr}$ and $Y_{im-corr}$ are the corrected real and imaginary parts of the admittance.

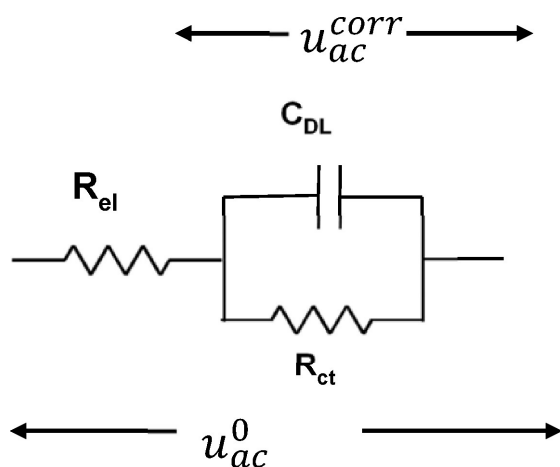


Figure 1. The equivalent circuit used for the simulation of C vs. E curves from AC voltammetry.

$$C_{diff} = \frac{Y_{im-corr}}{\omega}, \quad R_{ct} = \frac{1}{Y_{re-corr}} \quad (3)$$

Hence by utilizing $Y_{im-corr}$ for determining C_{diff} , it is possible to get the real value of the differential capacitance.

2. Theoretical

To support the interpretation of the experimental results, we employ a thermodynamic modelling framework which is capable to *predict* the non-linear behaviour of the double layer capacity.^[57] In this section we briefly sketch the most important aspects of the model and refer to^[58,59] for the detailed derivation.

The model is based on continuum non-equilibrium thermodynamics,^[68-70] where the liquid electrolyte is considered as a mixture of species A_α , $\alpha = 0, 1, \dots, N$, with space and time dependent molar densities $n_\alpha(x, t) = \frac{N_\alpha}{V} / \text{mol L}^{-1}$, where N_α is the number of constituents and V the volume of the mixture. With $\rho = \sum_{\alpha=1}^N m_\alpha n_\alpha$ we denote the mass density of the mixture, where m_α are the respective molar masses. We denote with μ_α the chemical potential of the corresponding species, which is derived from a free energy density $\rho \cdot \psi(n_0, \dots, n_N, E)$, where E denotes the electric field in the mixture, as

$$\mu_\alpha = \frac{\partial \rho \psi}{\partial n_\alpha}, \quad \alpha = 0, 1, \dots, N. \quad (3.1)$$

The free energy density $\rho \psi$ captures reference contributions of the pure substances, entropy of mixing contributions, mechanical contributions and polarization contributions, where the later one implies for the polarization vector

$$-P = \frac{\partial \rho \psi}{\partial E}. \quad (3.2)$$

Each constituent carries a charge $e_0 z_\alpha$, where the charge number can also be zero, e.g. for the solvent, which is typically denoted by A_0 , or A_s if we refer to a specific solvent, with $z_0 = 0$. The free charge density q of the electrolyte mixture is then

$$q = e_0 \sum_{\alpha=1}^N z_\alpha n_\alpha \quad (3.3)$$

and determines the electric field E via the Poisson equation

$$\epsilon_0 \partial_x (E + P) = q. \quad (3.4)$$

Note that a very important aspect of the model is the coupling to the stationary momentum balance

$$\partial_x p = q E, \quad (3.5)$$

where p is the internal pressure of the system at position x . The momentum balance (3.5) states that a pressure gradient is balanced by the electrostatic Lorenz force $q E$. The electric field

E is expressed as gradient of the electrostatic potential, in 1D thus $E = -\partial_x \phi$.

The chemical potential function μ_α for an incompressible mixture is considered as^[57–59]

$$\mu_\alpha = g_\alpha + k_B T \ln y_\alpha + v_\alpha p, \alpha = 0, 1, \dots, N, \quad (3.6)$$

where $y_\alpha = \frac{N_\alpha}{\sum_{\beta=0}^N N_\beta}$ denotes the mole fraction, v_α the partial molar volume of the constituent A_α , g_α the reference Gibbs energy of the constituent, and T the temperature. Note that the mole fraction y_α is defined with respect to the number density $N = \sum_{\beta=0}^N N_\beta$ of mixing particles and satisfies the condition $\sum_{\beta=0}^N y_\beta = 1$.

When solvation effects are present, there is a crucial difference between the total number of solvents molecules in solution, N_0^{tot} and the *free* or *unbound* number of solvent molecules which participate in the entropy of mixing, namely N_0 . We denote with κ_α the solvation number of constituent A_α , $\alpha = 1, \dots, N$, i.e. the number of solvent molecules bound to the central ion (see Figure 2). Hence, we have a relation

$$N_0 = N_0^{\text{tot}} - \sum_{\alpha=1}^N \kappa_\alpha N_\alpha \quad (3.7)$$

Due to the solvation effect, which is crucial to compute actually the number of free solvent molecules and its respective molar density.

But solvation does not only influence the entropy of mixing but also the partial molar volume v_α of an ionic species (see Figure 2). This has some very important consequences, since presumably v_α scales with κ_α and v_α arises in expressions of the coupled equation system. The incompressibility of the mixture entails a condition^[57]

$$\sum_{\alpha=1}^N v_\alpha n_\alpha = 1, \quad (3.8)$$

Which holds at each point in space. When v_α increases, the corresponding number density n_α has to decrease in order to ensure the condition (3.8). Consider as a simple example water, with $n_0 = 55.5/\text{mol L}^{-1}$ and thus $v_0 = \frac{1}{55.5}/\text{L mol}^{-1}$, as well as a solvated ion with $v_\alpha \approx \kappa_\alpha v_0$ due to the solvation effect. When only ions are present at some point in space, e.g. within the space charge layer of a metal-electrolyte interface, the incompressibility constraint (3.8) yields the maximum number density of the corresponding ionic species as $n_\alpha^{\text{max}} = \frac{1}{\kappa_\alpha v_0}$, which is about 1.8 mol L^{-1} for $\kappa_\alpha = 30$. This *saturation* is indeed found in space charge layers and has an important impact to the differential capacity of the double layer, which we briefly show.

Consider in a 1D setup an electrode, positioned at $x=0$ and some bulk position $x=x^{\text{bulk}}$ sufficiently far away from the electrode surface. Based on the above sketched model one is interested to compute the charge

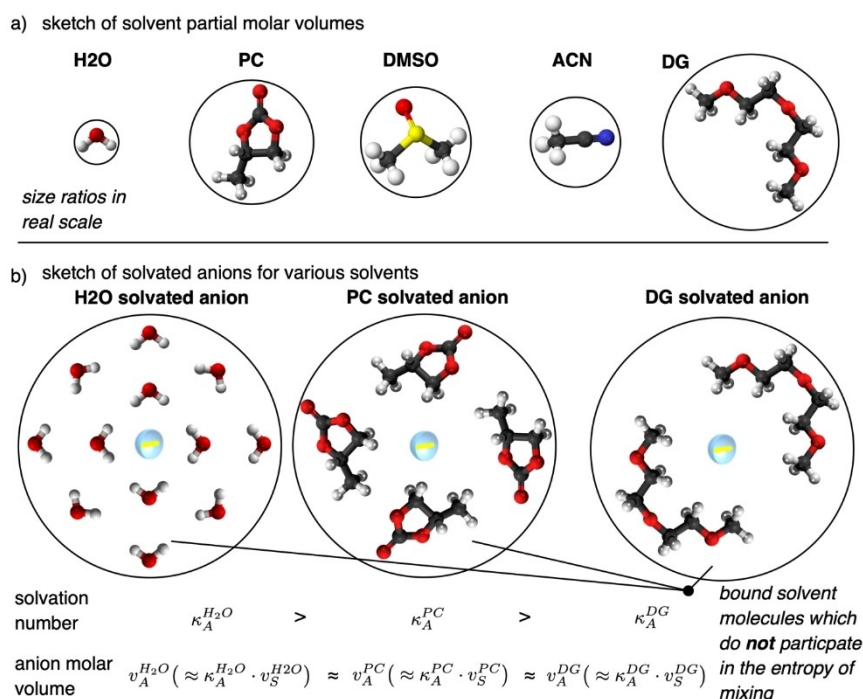


Figure 2. (a) Sketch of the partial molar volumes of various solvents considered in a spherical approximation (due to thermal motion). The size ratio is according to the ratio of molar volumes. (b) Sketch of solvated anions for different solvents which illustrates the impact of solvation on the partial molar volume. Different solvation numbers can lead to equally sized partial molar volumes of the solvated ion due to the different size of the solvent molecules. Further, bound solvent molecules do not participate in the entropy of mixing of the mixture.^[59] (Please note that different from usual textbook approaches the partial molar volume of the ions includes the volume of the solvation shell, and therefore the number of the solvent molecules is that of the unbound molecules. Also, volume differences of solvent molecules in the bound and unbound state are neglected.)

$$Q = \int_0^{x^{\text{bulk}}} q \, dx, \quad (3.9)$$

As function of the applied voltage $E = \varphi|_{x=0} - \varphi|_{x=x^{\text{bulk}}} + U^R$, where $U := \varphi|_{x=0} - \varphi|_{x=x^{\text{bulk}}}$ is the potential drop across the electrolytic space charge layer, and U^R a constant which captures the metal work function, the potential of the reference electrode, and so on.^[57] For non-adsorbing salts, the electrolytic charge in the electrolytic double layer consist only of the Q , i.e. no additional adsorbed electrolytic species on the surface.^[57] In^[57] it was shown that $Q = 0$ entails $U = 0$, whereby the measured voltage E_{pzc} is the potential of zero charge and equal to U^R , i.e. $E - E_{\text{pzc}} = U$. The differential capacitance is then obtained via $C = \frac{dQ}{dE}$. This can be achieved by considering (extended) diffusional equilibrium, i.e. $\partial_x(\mu_\alpha + e_0 z_\alpha \varphi) = 0$, $\alpha = 0, 1, \dots, N$, which yields with eq. (3.6) for the mole fraction

$$y_\alpha = y_\alpha^{\text{bulk}} e^{-\frac{e_0 z_\alpha}{k_B T}(\varphi - \varphi^{\text{bulk}})} - \frac{v_\alpha}{k_B T}(p - p^{\text{bulk}}) = y_\alpha(\varphi, p). \quad (3.10)$$

With the incompressibility constraint (3.8) we obtain

$$n_\alpha = \frac{y_\alpha(\varphi, p)}{\sum_{\beta=0}^N y_\beta(\varphi, p)} = n_\alpha(\varphi, p) \text{ and thus} \quad (3.11)$$

$$q = e_0 \sum_{\alpha=1}^N z_\alpha n_\alpha(\varphi, p) = q(\varphi, p)$$

The pressure contribution in the free charge density q is the central aspect of the series of papers,^[57–59] since it captures the effect of solvation and the increased partial molar volume of the ions. Comparing a simple Poisson-Boltzmann approach $y_\alpha = y_\alpha^{\text{bulk}} e^{-\frac{e_0 z_\alpha}{k_B T}(\varphi - \varphi^{\text{bulk}})}$ to the representation (3.10) clearly shows the crucial impact of pressure p and partial molar volume v_α . Note, however, that the solvation effect also impacts the actual value of y_α^{bulk} as described above.

Reinserting the representation (3.11) in the Poisson equation (3.4), together with $P = \varepsilon_0 \chi E$, where $\chi = \text{const.}$ is the dielectric susceptibility of the solvent, yields

$$-\varepsilon_0(1 + \chi) \partial_{xx} \varphi = q(\varphi, p). \quad (3.12)$$

This equation alone is not solvable, but requires in addition the momentum balance (3.5), i.e.

$$\partial_x p = -q(\varphi, p) \partial_x \varphi. \quad (3.13)$$

From the coupled equation system (3.12), (3.13), together with the representations (3.10) and (3.11) one is able to deduce an algebraic equation system to determine the boundary layer charge Q as function of the applied voltage U , i.e.

$$Q = \text{sgn}(U) \sqrt{2\varepsilon_0(1 + \chi)(p^0 - p^{\text{bulk}})}, \quad (3.14a)$$

$$g(U, p^0) := \sum_{\beta=0}^N y_\beta(U, p^0) - 1 = 0. \quad (3.14b)$$

With representation (3.10) of y_β . Note that there is a crucial difference between *classical* representations of $Q = Q(U)$ and the equation system (3.14a) and (3.14b), which requires a (numerical) solution of the implicit equation (3.14b) to determine $p^0 = p^0(U)$ and thus $Q = \text{sgn}(U) \sqrt{2\varepsilon_0(1 + \chi)(p^0(U) - p^{\text{bulk}})} = \hat{Q}(U)$. However, with modern numerical tools such as MATLAB or Python (scipy), this is straight forward. For the double layer capacity, we obtain finally the representation.^[57]

$$C = \frac{dQ}{dU} = -\text{sgn}(U) \sqrt{\frac{\varepsilon_0(1 + \chi)}{2(p^0 - p^{\text{bulk}})}} q(U, p^0). \quad (3.15a)$$

Which can be expressed as $C = \hat{C}(U)$ via solving the implicit equation (3.14b) as $p^0 = p^0(U)$.

Before applying this model framework to the experimental data, we briefly sketch some important aspects by representative numerical examples. For this, consider an arbitrary solvent of molar density n_s with molar volume v_s of the pure substance and dielectric constant χ , where a mono-valent salt AC is completely dissolved and dissociated. Note that incomplete dissociation can be crucial at higher concentrations due to the solvation effect.^[71] Figure 3 (left) shows the impact of the anion v_A and cation v_C partial molar volumes on the differential capacitance for water as solvent. Note that the capacity minimum is *independent* of $v_{A/C}$, while the *right* capacity maxima, i.e. positive of the potential of zero charge, depends on the molar volume of solvated anions v_A , while the *left* capacity maxima, i.e. negative of the potential of zero charge depends on the molar volume v_C of the solvated cations. Figure 3 (right) shows the corresponding space charge layers at an applied voltage of 1 V w.r.t. the potential of zero charge. The saturation concentration in the double layer is determined by the partial molar volume of the ions. The minimum is determined by χ and the salt concentration c . Figure 4 (left) shows a variation of the capacity for a range of salts of salt concentrations, while Figure 4 (right) shows computations of the capacity maximum with respect to the molar volume ratio between the solvated ions and the solvent, as well as with respect to the dielectric constant χ of the solvent.

Note that the ionic partial molar volumes v_A/v_C , the solvation numbers κ_A/κ_C , and the partial molar volume of the solvent v_s are certainly related to each other in some general way. It is of great interest to determine this relation on the basis of some microscopic theory, such as DFT or MD, as well as deduce it from experimental data. However, for the sake of this work we rely entirely on the relation

$$v_{A/C} = \kappa_{A/C} v_s \quad (3.16)$$

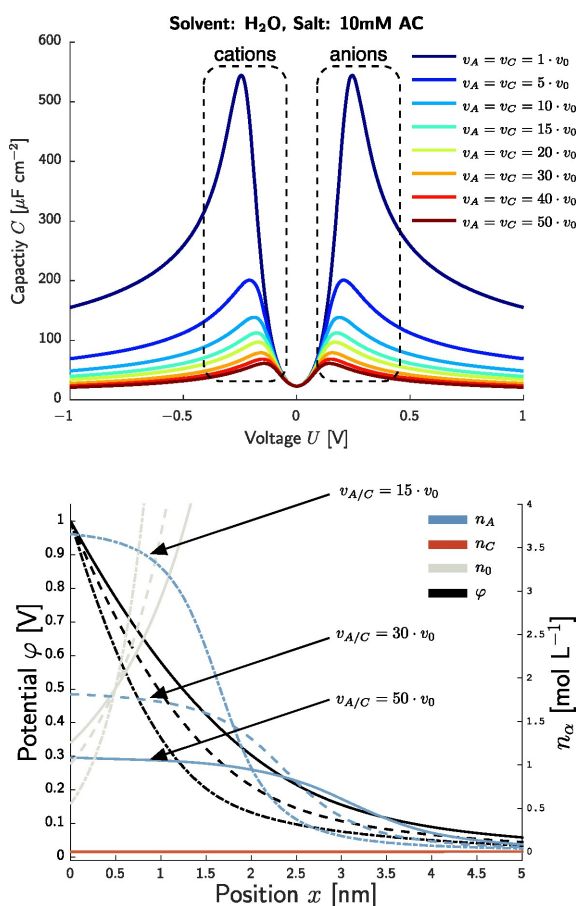


Figure 3. (left) Computed double layer capacity for water as solvent and various values of the partial molar volume v_A and v_C as multiples of partial molar volume v_0 of the solvent. (right) Structure of the space charge layer for different partial molar volumes $v_{A/C}$ at an applied voltage of $U = 1$ V. The saturation concentration of the anions in the space charge layer correlates with its partial molar volume.

for the ionic species, which allows us to interpret the experimental results in section 4 (see Figure 2 for a sketch of solvated ions of same size for different solvents and solvation numbers).

To investigate multi-valent ions, such as $\text{Ca}(\text{ClO}_4)_2$, one additionally has to question the dependency of the solvation number on the actual charge number, e.g. $\kappa_\alpha \sim |z_\alpha|^\gamma$. Then γ encodes the actual dependency, i.e. $\gamma = 0$ (solvation number is independent of the charge number), $\gamma = 1$ (solvation number is linear of the charge number), $\gamma = 2$ (solvation number is quadratically dependent on the charge number). Numerical calculations for each hypothesis will be shown below in section 3.3, which allow us to compare mono-valent and multi-valent perchlorates on the basis of this model.

Specific adsorption of ions entails a surface capacity C_s , which can be derived in a similar manner from surface thermodynamics. We refer again to^[57] for details as we consider for the sake of this work only non-adsorbing ions, even though they experimentally might occur, to focus on the contribution of the actual space charge layer in the electrolyte.

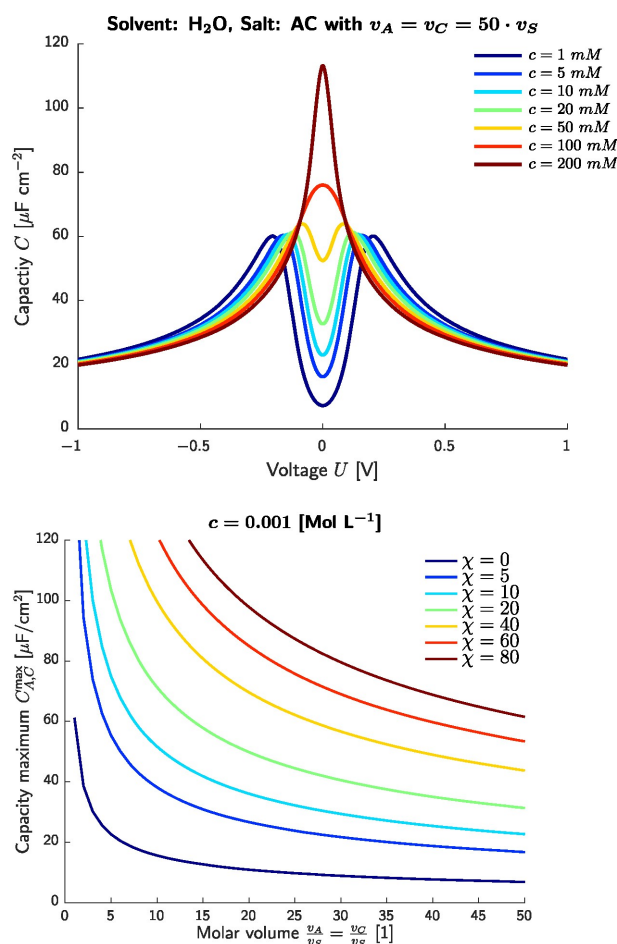


Figure 4. (left) Computed double layer capacity for water as solvent for various salt concentrations of a mono-valent salt, assuming $v_A = v_C = 50 v_0$. (right) Values of the capacity maximum as function of the molar volume ratio between the solvated ions and the solvent for various values of the dielectric constant χ .

The adsorption of solvent molecules A_s on the electrode surface Σ could lead to an additional potential U_s across this adsorption layer, which consists of two parts: (i) a contribution corresponding to the field within (potential drop across) an insulating dielectric layer which is dependent on the charge within the double layer and (ii) some contribution due to the oriented dipoles; their contribution at the pzc is comprised in E_{pzc} but their orientation may also depend on potential or double layer charge (cf. section 4.6), and only this latter effect is contained in U_s . The applied voltage E is hence related to the voltage drop $\varphi|_{x=0} - \varphi|_{x=x^{bulk}} = U$ across the electrolytic space charge layer as

$$E - E_{pzc} = U_s + U \quad (3.17)$$

Where the contribution of (ii) is incorporated in the constant E_{pzc} . Since U_s has to vanish at the potential of zero charge, we may write $U_s = U_s(Q)$, where Q is the charge stored in the electrolytic space charge layer.

Note that Q itself is actually dependent on U (see eqs. 3.14), whereby $U_s = U_s(Q(U))$. Within a linear approximation $U_s \approx \eta_s \cdot U$ we thus obtain

$$E - E_{pzc} = (1 + \eta_s) \cdot (\varphi|_{x=0} - \varphi|_{x=x^{bulk}}). \quad (3.18)$$

A more rigorous derivation and its embedding into the framework of non-equilibrium (surface) thermodynamics is given in a subsequent work and beyond the scope of this paper. It is important to note, however that this entails for the differential capacitance

$$C = \frac{dQ}{dE} = \frac{1}{1 + \eta_s} \frac{dQ}{dU} = \frac{1}{1 + \eta_s} \hat{C} \left(\frac{E - E_{pzc}}{1 + \eta_s} \right) \quad (3.19)$$

where $\hat{C}$ denotes the actual function derived from the equation system (3.14a, 3.15). Hence, η_s stretches the capacity curve, i.e. shifts the capacity maxima w.r.t. the potential, as well as decreases the capacity value, which is shown in Figure 5. We can relate η_s to the distance of the two capacity maxima, denoted as

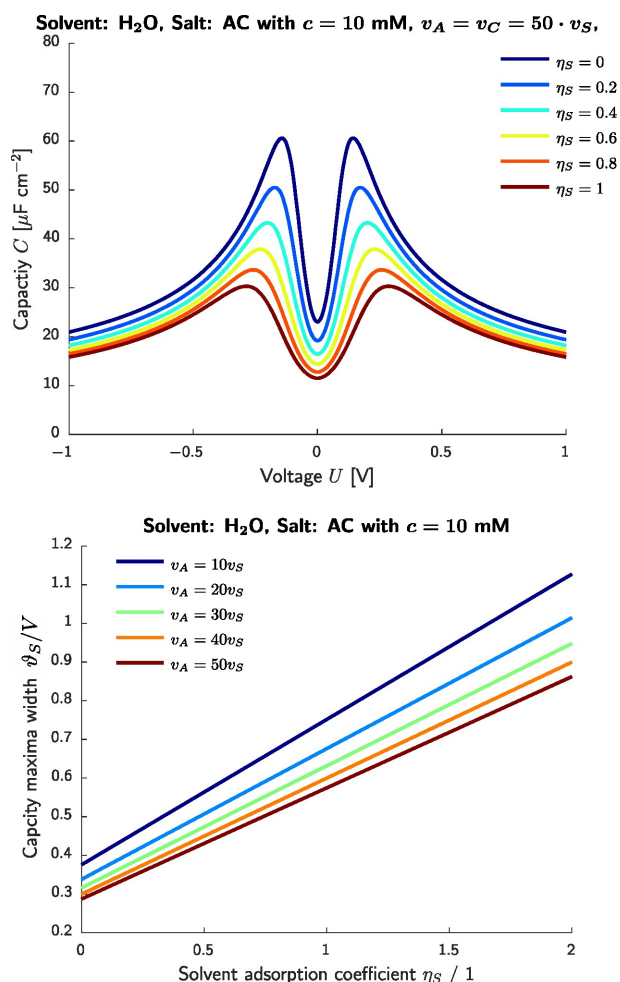


Figure 5. Impact of the solvent adsorption, encoded in the coefficient η_s on the capacity curve.

$$\vartheta_s := \varphi|_{c=c_{max}^+} - \varphi|_{c=c_{max}^-} = \vartheta_s(\eta_s) \quad (3.20)$$

and shown in Figure 5 (right) for various values of η_s , which we term *solvent adsorption coefficient* in the following. Eqs. (3.18) and (3.20) allow us to determine η_s and ϑ_s for the various solvents discussed in this work, without further specifying its microscopic theoretical origin, which is discussed in a subsequent work. In the light of Eq. (3.18), it is possible to show that

$$\vartheta_s = \vartheta_s^0 \cdot (1 + \eta_s), \quad (3.21)$$

where ϑ_s^0 is the potential width of the capacity maxima determined from the function $\hat{C}(U)$, i.e. for $\eta_s = 0$ (c.f. Figure 5 (left)). ϑ_s^0 is dependent on the partial molar volumes (v_A, v_C, v_S), the solvent specific susceptibility χ , and the salt concentration c . For given experimental data of ϑ_s it is thus possible to determine η_s .

The presented model framework is used in section 4 to interpret the measured experimental results on the basis of differential capacity curves. We emphasize here again that the overall model is subject to only a few unknown parameters, i.e. the partial molar volume of the anion and the cation as well as η_s . The potential and the concentration dependency of the differential capacity are self-consistently incorporated in the model framework.

3. Results and Discussion

3.1. Effect of the Solvent

The double-layer capacitance for different concentrations of KPF₆ on Au(111) electrode in the range 3 to 100 mM in DMSO and in the range 5 to 500 mM in PC, DG, and ACN is exhibited as a function of the potential in Figure 6 (A, B, C, and D), respectively. From the minima at the lowest concentrations we obtain the pzc values. They differ between the anodic and cathodic scan because during the anodic scan the surface is reconstructed. The reconstruction is lifted at positive potentials, and therefore the pzc values obtained in the cathodic sweep refer to the unreconstructed Au(111). In DMSO the difference is much less than in the other cases. Probably the anodic potential limit is not positive enough for a lifting of the reconstruction to be achieved. The pzc values in the positive direction which refer to freshly prepared reconstructed surface is higher than in the negative direction (unreconstructed surface) because the unreconstructed surface has a lower work function than the reconstructed one^[72,73]. The pzc values relative to DMFc scale changes as follows: ACN > DG > H₂O > PC > DMSO (Table 1).

Thus, the pzc is most positive in ACN and most negative in DMSO, and this behaviour is in good agreement with the pzc of polycrystalline gold in aprotic solvents^[34] where E_{min} values of gold (poly) and other metals (calibrated versus bis(biphenyl)chromium (BBCr(I/O) scale and mainly obtained from capacitance measurements) were summarized from literature data. For polycrystalline Au, they increase in the order MeOH < H₂O <

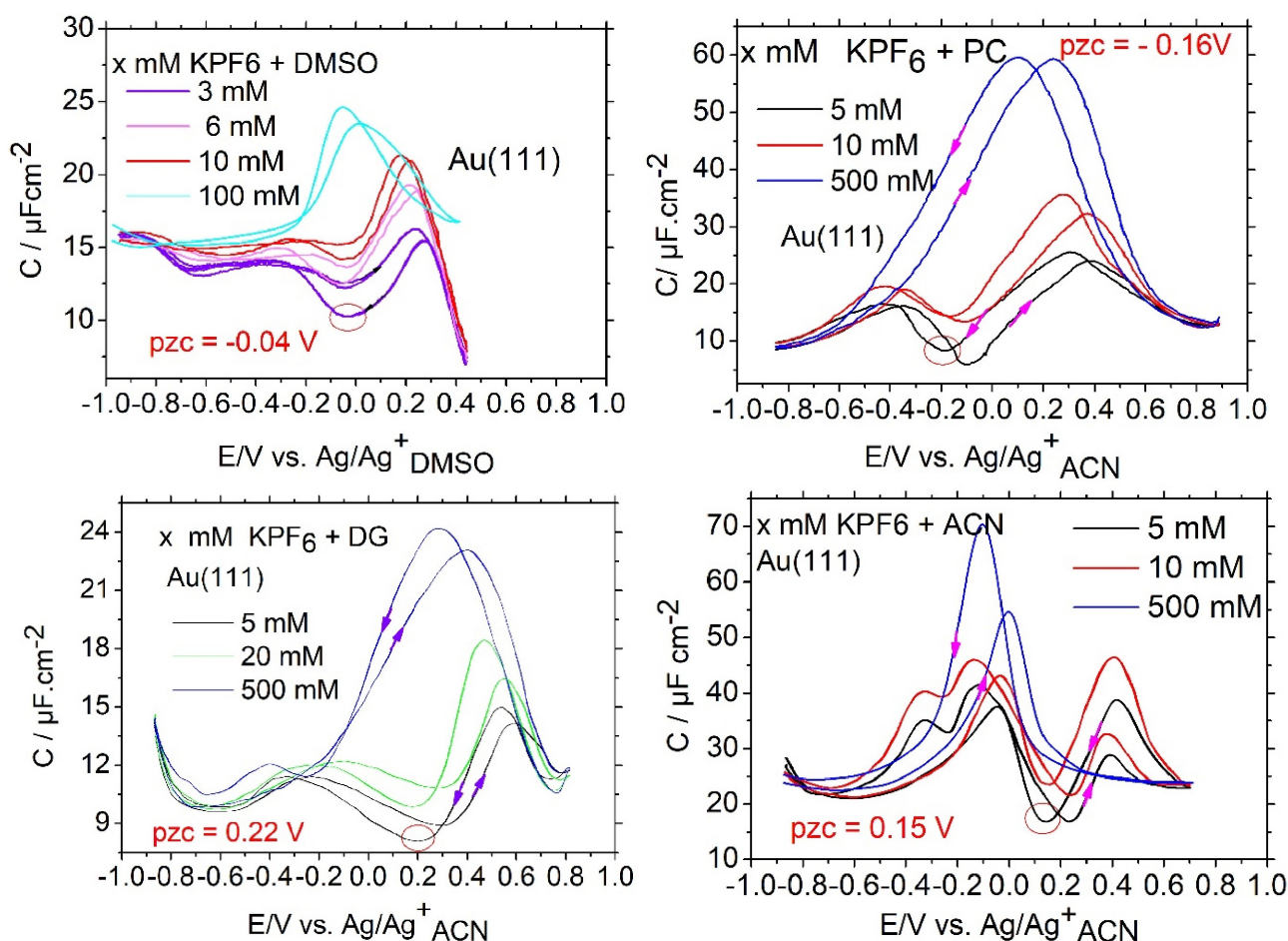


Figure 6. The differential capacitance of the double layer at Au(111) electrode in different concentrations solutions of KPF₆ in propylene carbonate (PC) (A), dimethyl sulfoxide (DMSO) (B), diglyme (DG) (C), and Acetonitrile (ACN) (D) at 10 Hz frequency, 3 mV r.m.s. the amplitude at a sweep rate of 10 mV s⁻¹.

Table 1. Physico-chemical properties of some organic solvents at 25 °C (KPF₆).

Solvent	pzc vs. Ag/Ag ⁺ Anod	pzc vs. Ag/Ag ⁺ Cath	pzc vs. DMFc*[V] Anod	pzc vs. DMFc*[V] Cath	ε ^[74,75]	n _D ^R [mol L ⁻¹]	ν ₀ [L ⁻¹ mol]	Donor number ^[74,76]	Polarizability α _s [10 ⁻³ nm ³] ^[34,34,77]	Dipole moment μ [D] ^[78]
DMSO	-0.01	-0.04	0.33	0.3	46.7	14.1	0.071	29.8	10.5	3.96
PC	-0.1	-0.16	0.4	0.32	69	11.8	0.085	15.1	9	4.9
DG	0.31	0.22	0.6	0.54	7.23	6.9	0.143	19.5	-	1.97
ACN	0.24	0.15	0.7	0.61	37.4	19.1	0.052	14.1	4.48	3.93
H ₂ O ^[14]	-	0.56 ^a	-	0.51	80.2	55.4	0.018	18	1.5	1.86

^a vs. SHE, pzc value in water vs. Fc/Fc⁺ = -0.06 V (0.56–0.624^[79]) and then it is converted vs. DMFc as following: = -0.06 + 0.57 (0.57 V is this difference between E_{1/2} for Fc and DMFc as in the literature^[80]).

DMSO < dimethylformamide < PC < ACN. The value of pzc of Au(111) in KPF₆ containing DMSO is -0.04 V (vs. Ag/Ag⁺) which is slightly different from that reported by Borkowska^[29] on the same electrode in DMSO containing LiClO₄ (pzc ~ 0.01 V vs. Ag/Ag⁺).

It is observed that the pzc values correlate neither with the dielectric constant of solvents nor with the solvent polarizability. Other factors like specific metal-solvent interactions and related to this, the donor number of the solvent will also play a role.^[40,47,55] A more detailed analysis involving the determination of the inner layer capacitance and in particular

solvent contribution would be necessary, as done for liquid metal electrodes like Hg in.^[81,82–84,55]

Theoretical Interpretation

The theoretical framework of section 3 (Theory) is used now to analyse the experimental results of differential capacity curves of the various solvents. We are especially interested in (i) determining approximately the ratio $\frac{V_{A/C}}{V_S}$ from the capacity maxima, (ii) estimating the solvent adsorption coefficients η_s from the measured capacity maxima width ϑ_s and the

computed value ϑ_s^0 , (iii) comparing subsequent a computation of the differential capacity (with the previously determined parameter) to experimental data on the whole voltage range, and (iv) comparing individual capacity curves for concentration variations.

The results of (i) and (ii) are summarized in table 2 and were determined from the data of 10 mM KPF₆ in the respective solvent (5 mM for DG). Due to the surface reconstruction of gold, the capacity is subject to a hysteresis between the forward and backward charging. We stick for our analysis to the backward (cathodic) branch to show the principal methodology. Note further again that specific adsorption of the ions is also neglected here, and $v_A = v_C$. Hence, the values in table 2 are considered as (best) approximations to the real values within this set of assumptions and the experimental error. Accounting more in detail for specific adsorption within the theoretical framework requires more refined data, which is subject to a subsequent work.

Surprisingly the molar volumes of the solvated ions $v_{A/C}$ are all the range of 1.5 L mol⁻¹, except for ACN, where $v_{A/C}$ is three times smaller. Relating this to the solvation number $\kappa_{A/C}$ by the simple relation (3.8), i.e. $v_{A/C} \approx \kappa_{A/C} v_s$, which states that the partial molar volume of the solvated ion is essentially determined by the $\kappa_{A/C}$ solvent molecules, leads the values $\kappa_{A/C} = \frac{v_{A/C}}{v_s}$ in Table 2. Note, however, that packing densities or variations of the solvent molar volume within the solvation shell are not considered here. We can also deduce an equivalent radius $\hat{r}_{A/C}$, assuming spherical shaped solvated ions, from the partial molar volume via^[79] $v_{A/C} = \frac{4\pi}{3} \hat{r}_{A/C}^3$, and the corresponding values are given in Table 2. In accordance with Ref. [79], we find a clear deviation to the Stokes radius (c.f. Table 3) which originates from the solvation effect.

Figure 7 shows a comparison between the experimental capacity data of KPF₆ and the theoretical computation for the various solvents in the experimental voltage range. Given the stated assumptions, the broad accordance is remarkable and indicates that the differential capacity is a versatile tool to screen the thermodynamic properties of different solvents in the electrolytes of the same salt.

	PC	DMSO	DG	ACN	H ₂ O
$\frac{v_{A/C}}{v_s}$	20	25	10	10	70
$v_{A/C}$	1.7/L mol ⁻¹	1.8/L mol ⁻¹	1.4/L mol ⁻¹	0.52/L mol ⁻¹	1.3/mol L ⁻¹
$\hat{r}_{A/C}$	8.76 Å	8.93 Å	8.22 Å	5.91 Å	8 Å
ϑ_s	0.51/V	0.41/V	0.64/V	0.37/V	0.28/V
η_s	1.02	0.68	1.56	0.15	0.03

cation	r_{Stokes}^a [Å]	C_{max} (5 mM)	pzc V vs. DMFc (Cath)
Li ⁺	3.82	19.2	0.67
K ⁺	3.31	26	0.68
Ca ⁺²	4.12	16.3	0.66

^a Corrected Stokes radius of the ion as described in Ref. [92]

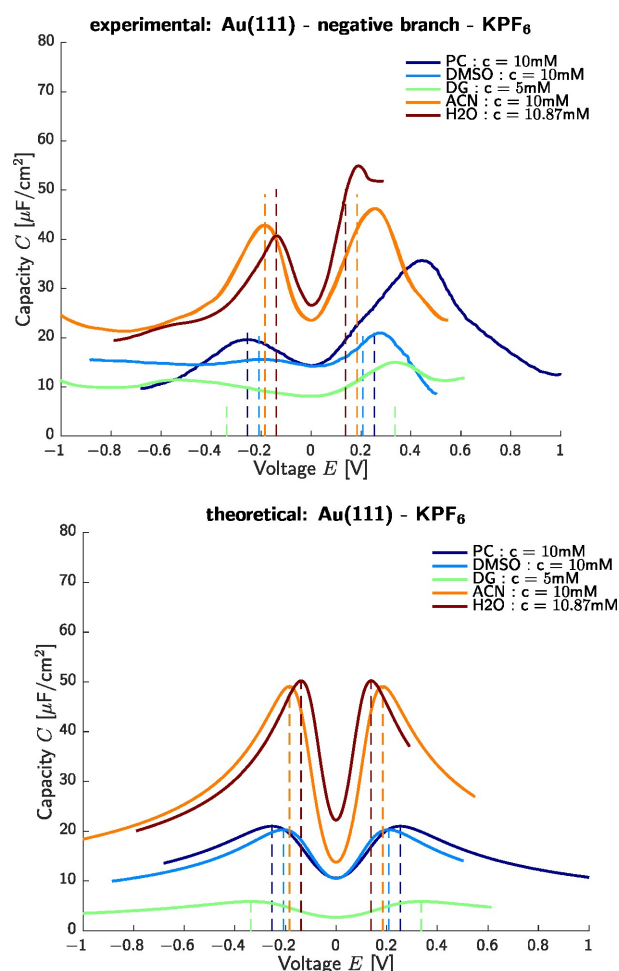


Figure 7. Comparison of the experimental data (left) for Au(111) | 10 mM KPF₆ (5 mM for DG) and theoretical data (right).

Figure 8 shows computations for DG (left) and ACN (right) for a range of concentrations. A comparison to Figure 2 shows a coincidence in the concentration dependency.

3.2. Effect of the Anions

The effect of the specific anion adsorption on Au(111)|electrolyte interface in the organic solvent (DMSO) was studied with potassium salts in DMSO. The results obtained are shown in Figure 9 (A and B). The negative shift of the pzc in the case of Br⁻ adsorption compared to that for PF₆⁻ is typical for strong adsorption. The peak positive of the pzc is attributed to the adsorption of Br⁻ and PF₆⁻ (-0.5 and 0.28 V vs. Ag/Ag⁺, respectively).^[85] In the case of KBr salt, the molar volume of anion and cation have a similar size because the two capacitance maxima are almost the same. So one can conclude that monovalent cation and anions in DMSO have the same partial molar volume. Compared to KPF₆ salt in aqueous solution on Ag(110):^[85] At 0.01 M left, C (max) ~50 μF.cm⁻² (cation), while at 0.01 M of KBr in DMSO, the left C(max) ~30 μF.cm⁻² (cation). From this, it can be concluded that the

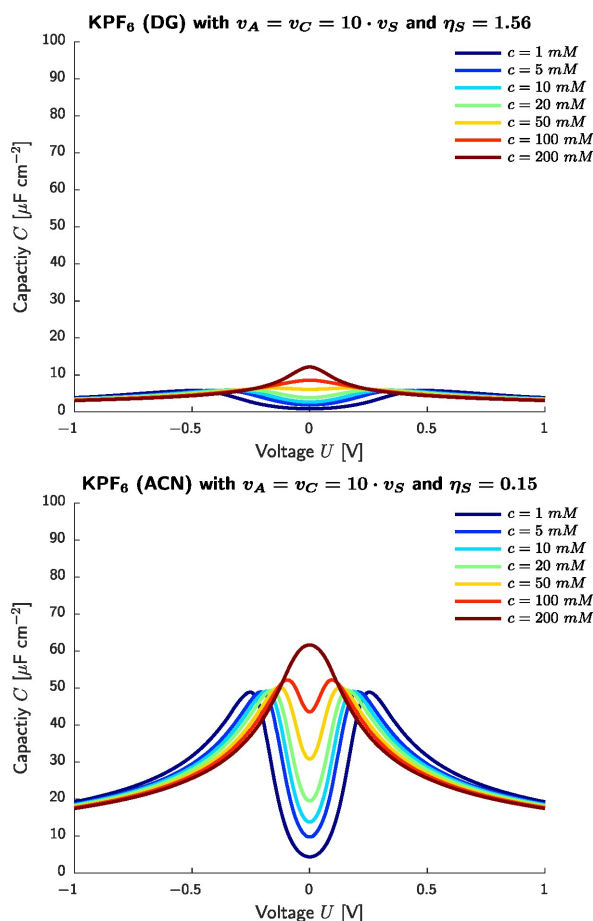


Figure 8. Computation of KPF₆ solutions in DG (left) and ACN (right) for various concentrations.

partial molar volume of cations in DMSO is much larger than in water.

Similar to Au(111) electrodes in aqueous solutions,^[86,87] the anodic capacitance maximum increases in the order: Cl[−] < Br[−] <

I[−] and this is attributed to adsorption strength. This trend is like anion adsorption activity on Bi(hkl) in organic solvents.^[88] Bromide is more specifically adsorbed than PF₆[−] so pzc shifts to a more negative potential. While the pzc of Au(111) in the case of ClO₄[−] is quite similar to PF₆[−] as shown in Figure 10.

The clear capacitance minimum and the small distance of the capacitance maxima for low concentrations in the case of bromide deserves special attention. First, for a strongly adsorbing ion like bromide we would not expect a capacitance minimum at all: bromide desorbs at such potentials, i.e. so far negative of the pzc in absence of specific adsorption, where the surface concentration of the cation is large and therefore also its contribution to the capacitance. (Note: the minimum in capacitance observed in^[24] for Ag(110) in bromide containing electrolyte is due to two separate Br[−] adsorption processes.) Second, such a clear, narrow capacitance minimum seems to suggest that the solvent is not adsorbing on the surface and thus not forming an additional layer. We have already shown previously that the adsorption/desorption of bromide is very slow in organic electrolytes.^[89] From the impedance spectra shown there we expect that the bromide coverage does not follow the 10 Hz ac signal used in this work for the determination of the capacitance. Rather, at this frequency, instead of determining the change of the total charge from the capacitance, we measure the capacitance corresponding to the change of the free charge only. Therefore, the minimum observed should correspond to the point of zero free charge (pzfc) of a bromide modified electrode surface. This situation is then similar to the case of a Pt(111) electrode modified by a monolayer of Ag, where the pzc is shifted exactly to a value expected from the work function of a Ag monolayer on Pt.^[90] A further effect of this strongly adsorbed bromide adlayer is that it prevents adsorption of the solvent molecules. This could explain that the broadening of the minimum is not observed in this case. However, we have to take into account that the Br[−] coverage certainly is dependent on potential, and slowly adjusting to the equilibrium value during the potential sweep.

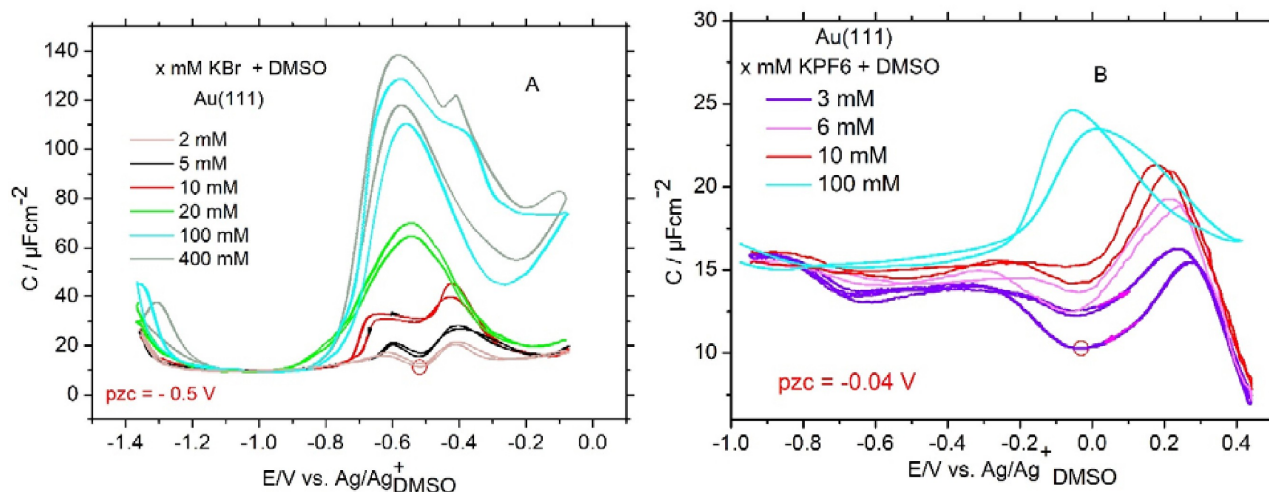


Figure 9. C(E) curves for Au(111) electrode in DMSO containing different anions: (A) Br[−] and (B) PF₆[−] at 10 Hz frequency, 3 mV r.m.s. the amplitude at a sweep rate of 10 mVs^{−1}.

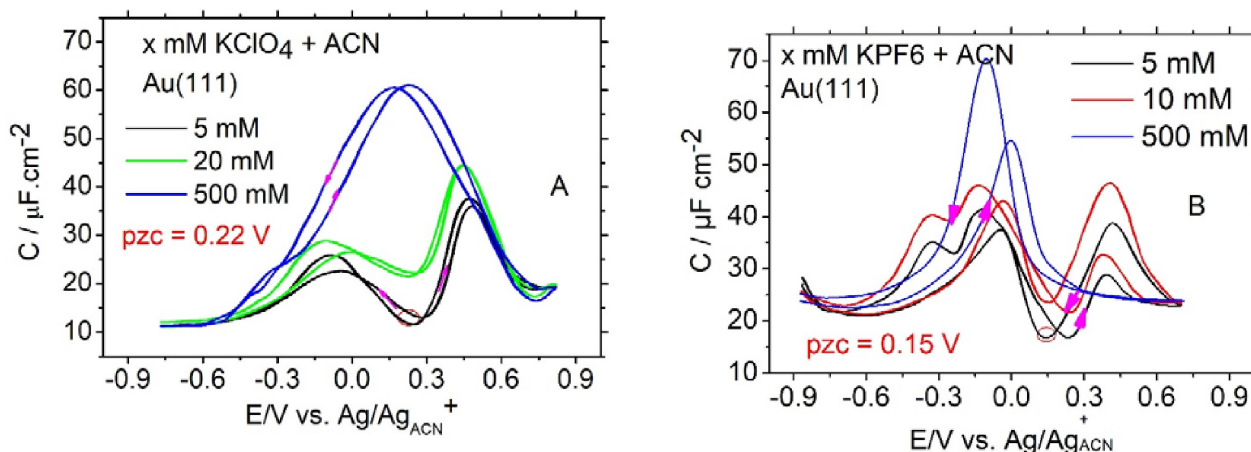


Figure 10. C(E) curves for Au(111) electrode in ACN containing different anions: (A) ClO_4^- and (B) PF_6^- at 10 Hz frequency, 3 mV r.m.s. the amplitude at a sweep rate of 10 mV s^{-1} .

Therefore, the above observation for bromide and the explanation is only preliminary and further work is necessary.

Theoretical Interpretation

Figure 11 shows experimental data of Valette for various concentrations of KPF_6 , KBF_4 and NaClO_4 with water as solvent in contact with Ag(110) electrode. Note that ClO_4^- is subject to slight adsorption whereby the capacity hump is a superposition of space charge layer capacity and adsorption capacity.^[57] The most important observation for this section is the circumstance that the capacity maxima for the anions (positive of the potential of zero charge) of PF_6^- , BF_4^- and ClO_4^- (taking into account the surface adsorption of ClO_4^-) are the almost equal. This entails almost equal values for the partial molar volume of the solvated anions with water as solvent, and we seek to answer the question whether this also the case for different solvents.

Exemplarily we discuss ACN as solvent in the following on the basis of the model framework of section 3. Figure 12 shows a comparison of the differential capacity for various salt

concentrations of KClO_4 (Left) and KPF_6 (Middle). As shown in section 3.2, the right capacity hump encodes the partial molar volume of the anion. For ACN-solvated ClO_4^- and PF_6^- we find similar values for the capacity maxima (within the experimental error), which leads to the conclusion that $v_{\text{ClO}_4^-} \approx v_{\text{PF}_6^-}$. Figure 12 (right) shows a computation of the corresponding capacity for the value of $v_{\text{A}^-} = 10 \cdot v_{\text{ACN}}$ and $\eta_s = 0.15$ (c.f. section 4.1). Note that the reduced capacitance maxima for high salt concentrations of the experimental data compared to the theoretical model might be due to incomplete dissociation arising from the solvation effect.^[71] Our findings indicate that similar to water also for aprotic solvents the partial molar volume of mono-valent anions is (almost) independent of the specific central ion and a fixed value which depends, however, on the solvent. Assuming that the solvation number is simply related to the molar volume by $v_{\text{A}^-} = \kappa_{\text{A}^-} \cdot v_{\text{ACN}}$, we would deduce $\kappa_{\text{A}^-} = 10$.

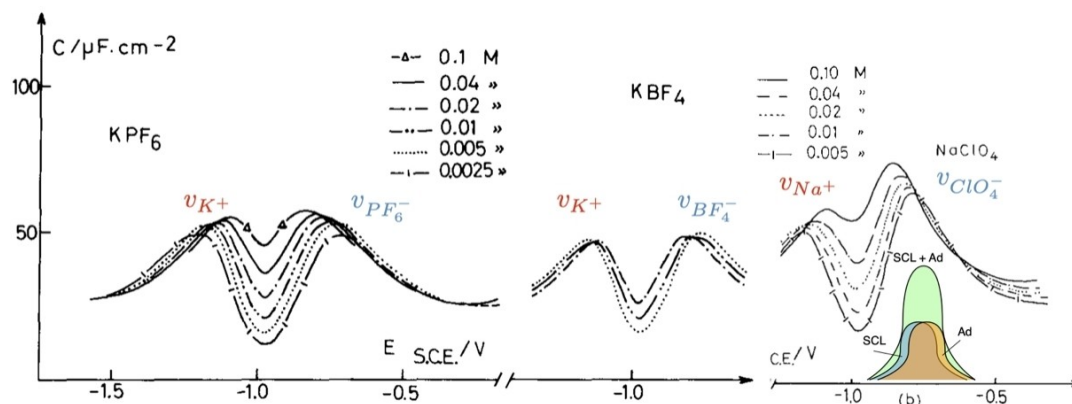


Figure 11. Data of Valette.^[85] Lower right: Sketch of the capacity superposition due to the space charge layer and the surface adsorption.

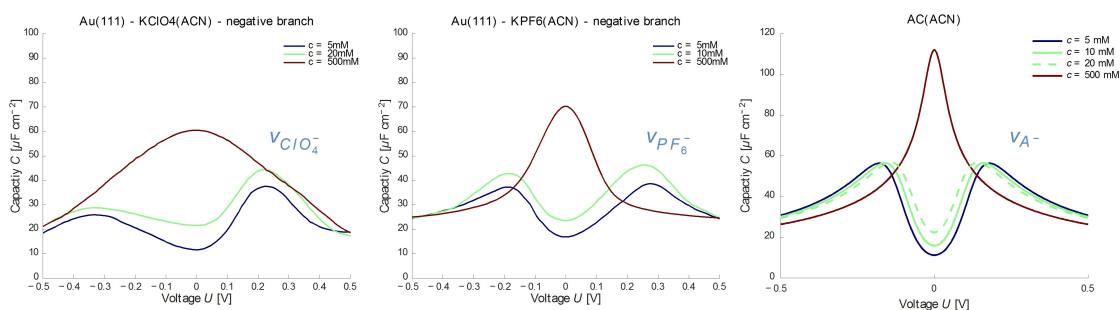


Figure 12. Differential capacity for various salt concentrations. (Left) Experimental data for KClO_4 , (middle) Experimental data for KPF_6 , (right) theoretical computation.

3.3. Effect of the Cations

It is well established that the thickness of the interfacial double layer is dependent on cation size.^[4,91] The differential capacitance curves measured for organic solutions of monovalent cations (Li^+ and K^+) and divalent cation (Ca^{2+}) with the same anion (ClO_4^-) of salt in contact with acetonitrile are presented in Figure 13 (A, B, and C), respectively.

The curves practically converge at the negative potentials limit independent of the cation with a value of about $10 \mu\text{C cm}^{-2}$. At less negative charges, the capacitance maximum increases in the order $\text{Ca}^{2+} < \text{Li}^+ < \text{K}^+$ in accordance with

corrected Stokes radii derived by Nightingale,^[92] (Table 3). The capacitance value at the negative potential limit varies from $10 \mu\text{F cm}^{-2}(\text{Li}^+)$ over $11 \mu\text{F cm}^{-2}(\text{Ca}^{2+})$ to $12 \mu\text{F cm}^{-2}(\text{K}^+)$ and for the monovalent cations has a similar dependence as for the $\text{Hg}|\text{DMSO}$ interface for 0.1 M solutions^[41,69] and for the Hg interface with aqueous electrolytes (0.1 N).^[93] The data of the C(E) curves are summarized in Table 3. The capacitance (C) at large negative charges ($C \sim 10.5 \mu\text{F cm}^{-2}$) closely agrees with values obtained for other electrodes materials (Bi, Ln + Ga, and Hg) in ACN.^[47] The values of pzc are practically independent of the cation similar to observed on Au(111) in aqueous

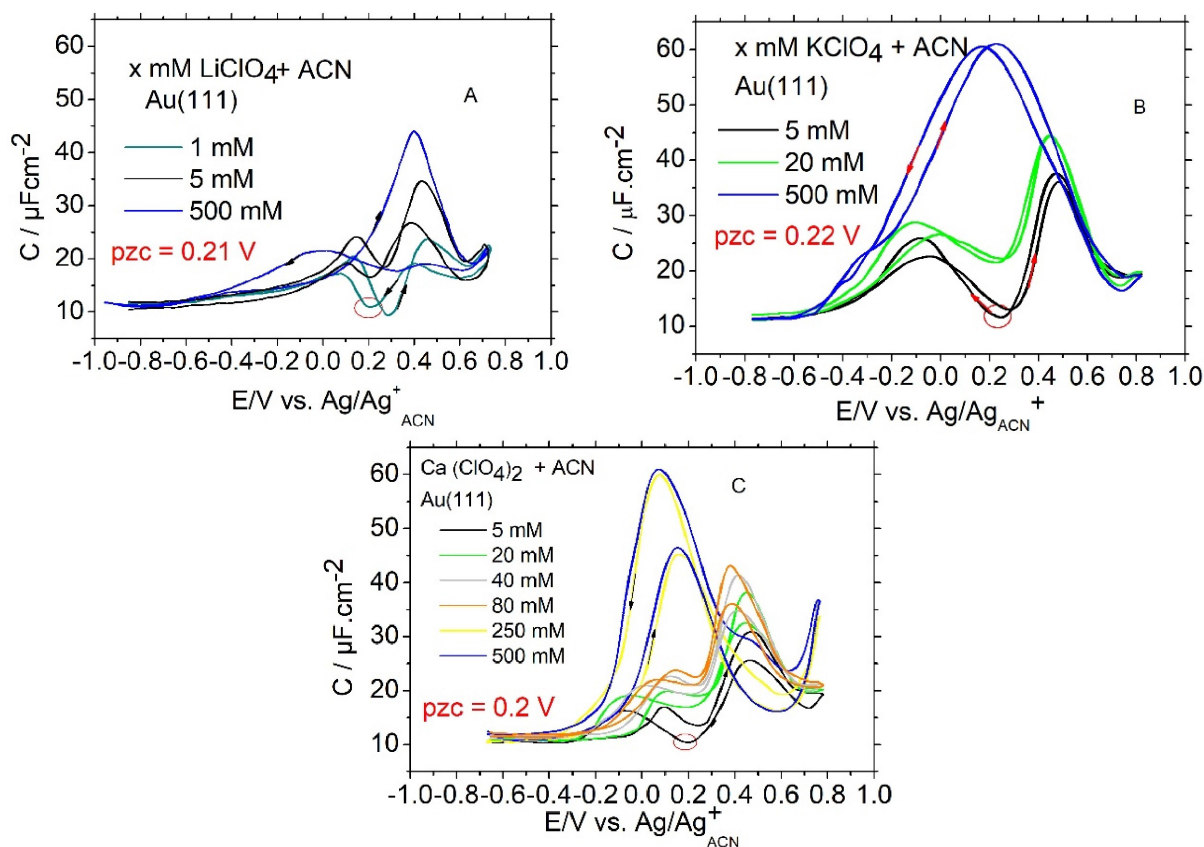


Figure 13. C(E) curves for Au(111) electrode in acetonitrile (ACN) containing different cations: (A) Li^+ , (B) K^+ , and (C) Ca^{2+} at 10 Hz frequency, 3 mV r.m.s. amplitude at a sweep rate of 10 mV s^{-1} .

solution.^[94] Since 250 mM and 500 mM almost no longer differ, the salt is no longer completely dissociated.

Theoretical Interpretation

The discussion was yet based on salts consisting exclusively of mono-valent ions. When ions of higher valency are considered, the question arises if the partial molar volume (and thus the solvation number) scales with the charge number of the ion. We consider thus exemplarily an ACN solution with some mono-valent salt AC and a multi-valent salt A_2C . Based on the observation that $v_{C^+} \approx v_{A^-}$ for mono-valent ions, we consider three models for the partial molar volume of the multi-valent ion C^{2+} , (i) $v_{C^{2+}} \approx v_{A^-}$, (ii) $v_{C^{2+}} \approx |z_{C^{2+}}| \cdot v_{A^-}$ and (iii) $v_{C^{2+}} \approx |z_{C^{2+}}|^2 \cdot v_{A^-}$.

For all three models we can compute the differential capacity (Figure 14 (left)) and compare the computation to the experimental data of the series of $LiClO_4$, $KClO_4$, and $Ca(ClO_4)_2$ with ACN as solvent (Figure 14 (right)).

We observe that the left capacity maximum of the series $LiClO_4$, $KClO_4$, and $Ca(ClO_4)_2$ is in the same order, and especially the capacity hump for Ca^{2+} not larger than the capacity humps

for Li^+ and K^+ . This is a first indication that the partial molar volume of multi-valent ions scales with the square of the charge number, i.e. $v_{C^{2+}} \approx |z_{C^{2+}}|^2 \cdot v_{A^-}$. Translating this back in terms of the solvation number would entail $\kappa_a \sim |z_a|^2$ for some ion species A_a .

3.4. Effect of Water on the PZC

Because water is the key impurity in aprotic solvents, investigating its effect on the interfacial capacities in general and particularly the capacitance is crucial. As seen in Figure 15, capacitance values increase with raised water concentrations from 1.28 to 58 mM whereas the shape remains largely unchanged. The potential of the capacitance minimum i.e., the pzc, changes to more positive values. This trend is identical to that obtained by Petrii and Khomchenko on Pt (poly)/acetonitrile^[36] and on Au (poly) in PC.^[32] Such capacitances increase with rising water content, were also observed for the Au(111) electrode in the ionic liquid in the positive potential region.^[95]

3.5. Effect of the Surface Structure of the Au Electrode on the PZC

The effect of the atomic arrangement of the electrode surface on the double layer characteristics is well established.^[20,29,72] The capacitance-potential curves for the gold (111) and roughened (111) surfaces in acetonitrile and propylene carbonate at various $LiClO_4$ and KPF_6 concentrations are presented in Figures 16 and 17, respectively. Also, C, E curves for Au(111), and polycrystalline gold electrode in different concentrations of KPF_6 containing DMSO are exhibited in Figure 18.

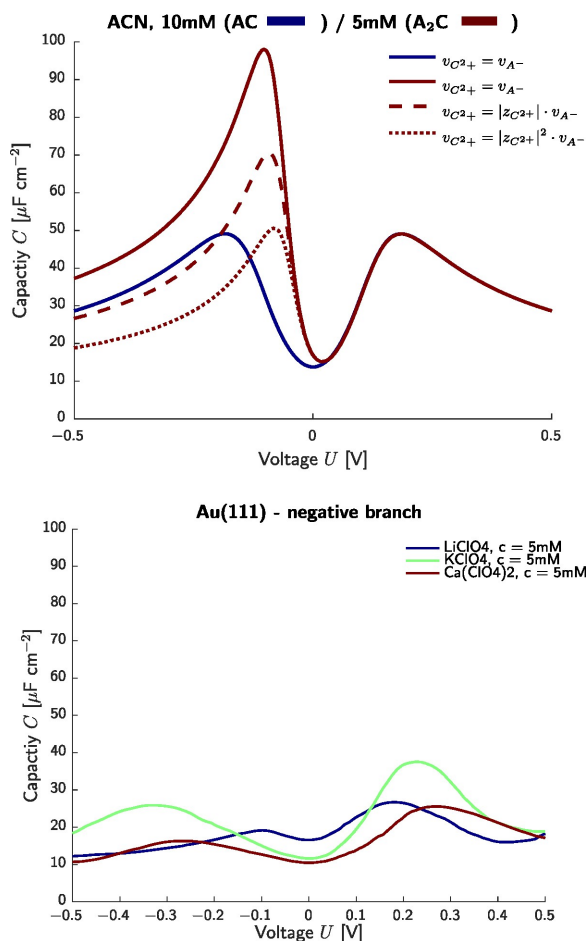


Figure 14. (Left) Computed differential capacity for a mono-valent salt AC and a multi-valent salt A_2C for various models of $v_{C^{2+}}$. (Right) Experimental data for $LiClO_4$, $KClO_4$, and $Ca(ClO_4)_2$ in CAN.

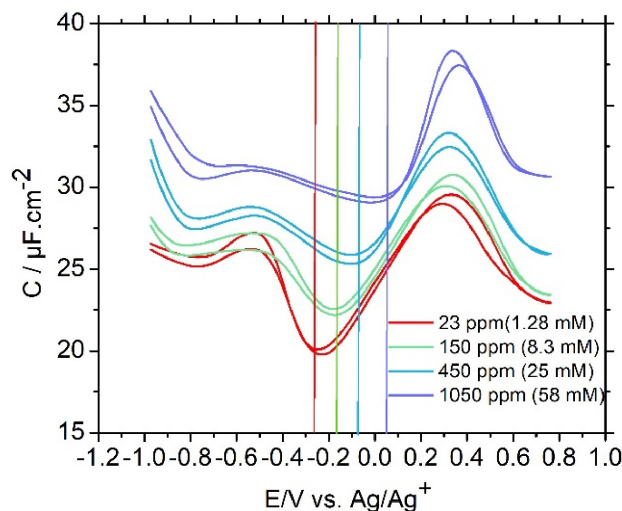


Figure 15. Curves of the differential capacitance of the roughened Au (111) electrode in propylene carbonate solutions of 10 mM KPF_6 , and with additions of 150, 450, and 1050 ppm of water using an AC perturbation of 10 Hz frequency, 3 mV r.m.s. the amplitude at a sweep rate of 10 mVs⁻¹.

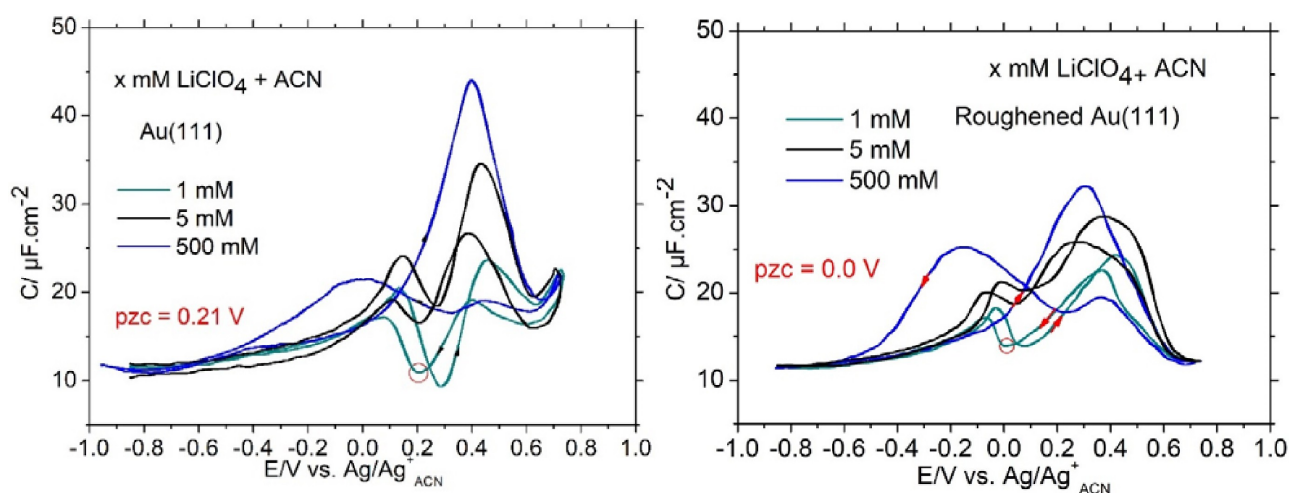


Figure 16. C(E) curves for Au(111) and roughened Au(111) electrode in ACN solutions in different concentrations of x mM LiClO_4 (as shown in the figure) using an AC perturbation of 10 Hz frequency, 3 mV r.m.s. the amplitude at a sweep rate of 10 mV s^{-1} .

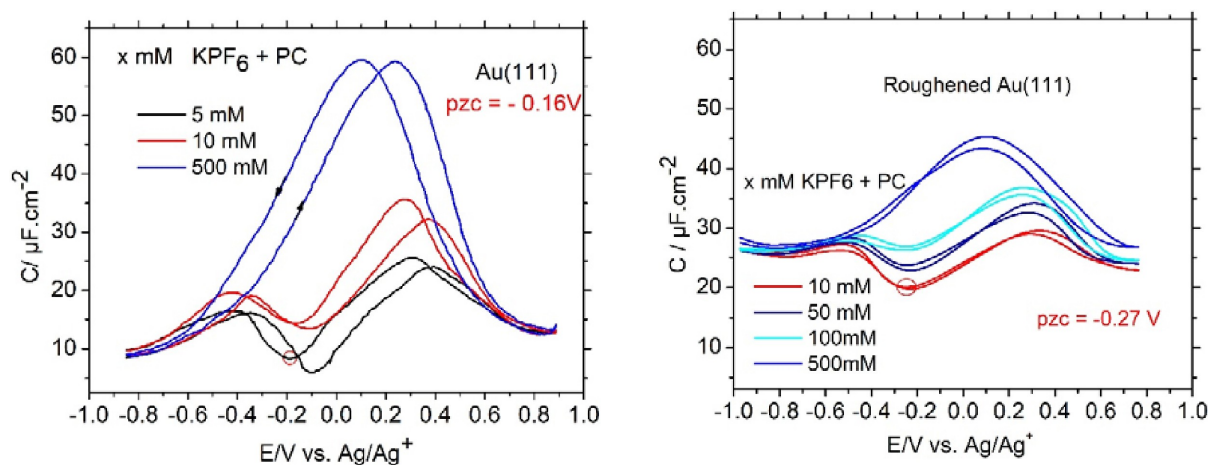


Figure 17. Same as in Figure 16, but in KPF_6 + Propylene carbonate.

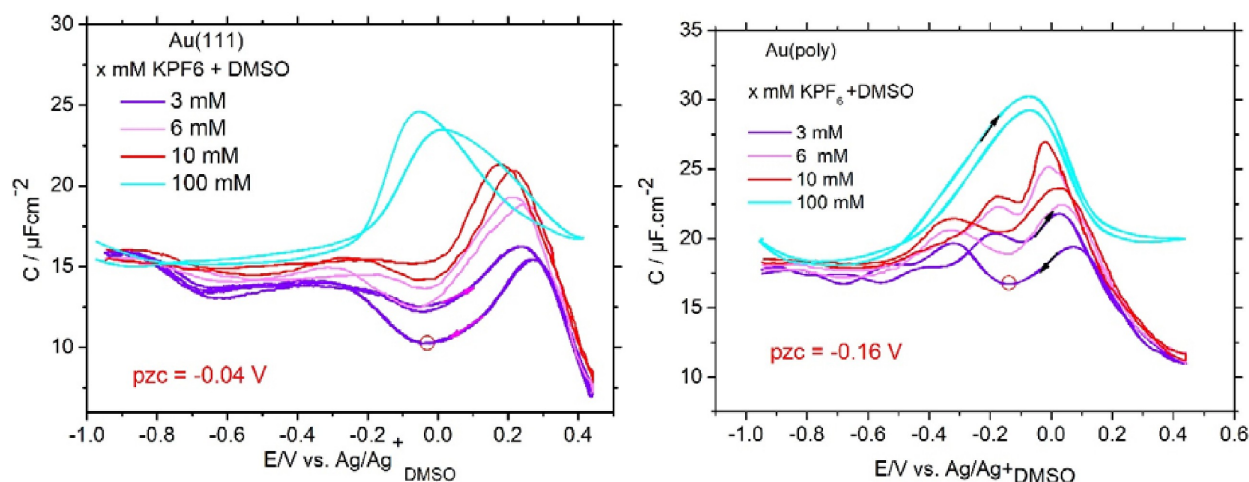


Figure 18. C(E) curves for a (111) and polycrystalline gold electrode. Concentration dependence in KPF_6 solutions in DMSO.

Both electrodes display a similar behavior. For both, the capacitance curves show a minimum at low concentrations. The same trend is found for KPF₆ in DMSO solutions. At a minimum, capacitance grows with salt concentration due to the concentration-dependent contribution of the diffuse portion of the double layer, confirming that the minimum can be regarded as pzc.^[18,29] The potential (E_{pzc}) varies from experiment to experiment within ± 11 mV for independent experiments for changing salt concentration, which displayed no systemic variability with the salt concentration. The pzc remains approximately constant with concentration variation as reported in the literature for Au(111) and Ag(111) electrode in aqueous solution.^[22,94]

The capacitance value at the minimum, C_{min} , increases at the roughened surface (for instance, minimum capacitance for Au(111) and polycrystalline-Au equals 10.2 and 16.6 $\mu\text{F}\cdot\text{cm}^{-2}$ (KPF₆ in DMSO), resp.). This cannot be explained by the increased roughness factor of the roughened electrode of 1.1 and therefore is due to the more open atomic arrangement, similar to the increasing capacitance observed at the 111, 100, and 110 faces of the silver electrode in aqueous electrolyte.^[20]

It is well known that the pzc of metal electrode and the work function φ_{M} are directly interrelated.^[8,96,97] The difference in the potential of zero charge between the Au(111) and the roughened Au(111) electrodes in LiClO₄ containing ACN ($E_{\sigma=0} = 0.21$ V and 0.0 V, respectively), in KPF₆ containing PC ($E_{\sigma=0} = -0.16$ V and -0.27 V, respectively) and in KPF₆ containing DMSO ($E_{\sigma=0} = -0.04$ V and -0.16 V, respectively) corresponds closely to the difference in the work functions of the reconstructed (111) gold surfaces and polycrystalline gold electrode ($\varphi_{\text{Au-PC}} = 5.11$ and $\varphi_{\text{Au(111)}} = 5.3$).^[73,98] Table 4 Summarizes the values of pzc of Au(111) electrode in different organic solvents, referenced against standard reference electrode (DMFc) to minimize complications due to uncertain liquid junction potentials.

3.6. Surface-Enhanced Infrared Absorption Spectroscopy (SEIRAS)

The electrode/ electrolyte interface was investigated in an organic solvent by using SEIRAS. Infrared spectra of PC adsorbed on a gold surface at different potentials in the presence of 0.1 M KClO₄ are shown in Figure 19 (A and B). The corresponding cyclic voltammogram of the system is exhibited in Figure 19C. The reference spectrum has been taken at 0.4 V. The bipolar band at about 1805 cm^{-1} corresponds to the C–O vibration of PC which was measured on silver electrodes in presence of NaI in SERS measurement.^[99] With more negative potentials, it shifts to lower wavenumbers. The intensity increases with more negative potential due to the increasing field strength and the resulting stronger orientation of the PC molecules. The negative band due to the subtraction of the reference spectrum becomes more prominent at more negative potentials because of the larger frequency shift. The system behaves reversibly. Except for a small broad peak at -0.2 V (i.e. in the vicinity of the pzc), the resulting CV at the potential limit 0.4–1.0 V is fairly featureless. The band at 2338 and 2364 cm^{-1} in Figure 19B corresponds to the asymmetrical stretching vibration band of CO₂ in the gas phase; this is caused by the changing CO₂ content in the spectrometer setup. Figure 20 (A and B) shows IR spectra for gold thin layer film covered by iodide at two different reference spectra (-0.4 and -1.8 V, resp.) and recording cyclic voltammogram recorded during spectra obtaining (Figure 20 C). The presence of iodide in the electrolyte (Figure 20) shifts the pzc to -1.1 V. Changing the potential in a more positive direction leads to a stronger field and, thus, stronger alignment of the PC molecules. The absence of a negative band in Figure 20 B suggests that the intensity at -1.8 V is very small. Also in Figure 19 B, the absorbance decreases from its maximum value around -1.0 V to lower values. We expect that the status of the surface with and without iodine is the same at the negative potential limit because no anions are adsorbed. Further experiments, e.g. with varied cations, might solve this question.

Table 4. Values of pzc of Au(111) and roughened electrode in different organic electrolytes.

Electrolyte	Solvent	Electrode	pzc/V vs. Ag/Ag ⁺ (Cath)	pzc/V vs. DMC [*] (Cath)
KPF ₆	PC	Au(111)	−0.16	0.32
KPF ₆	PC	r. Au(111)	−0.27	0.21
KPF ₆	DMSO	Au(111)	−0.04	0.3
KBr	DMSO	Au(111)	−0.5	−0.16
KPF ₆	DG	Au(111)	0.22	0.54
KPF ₆	ACN	Au(111)	0.15	0.61
LiClO ₄	ACN	Au(111)	0.21	0.67
LiClO ₄	ACN	r. Au(111)	0.0	0.46
LiClO ₄	PC	Au(111)	−0.17	0.31
Ca(ClO ₄) ₂	ACN	Au(111)	0.2	0.66
KClO ₄	ACN	Au(111)	0.22	0.68
KClO ₄	PC	Au(111)	−0.21	0.27
KPF ₆	DMSO	poly.(Au)	−0.16	0.18

* r means a roughened electrode

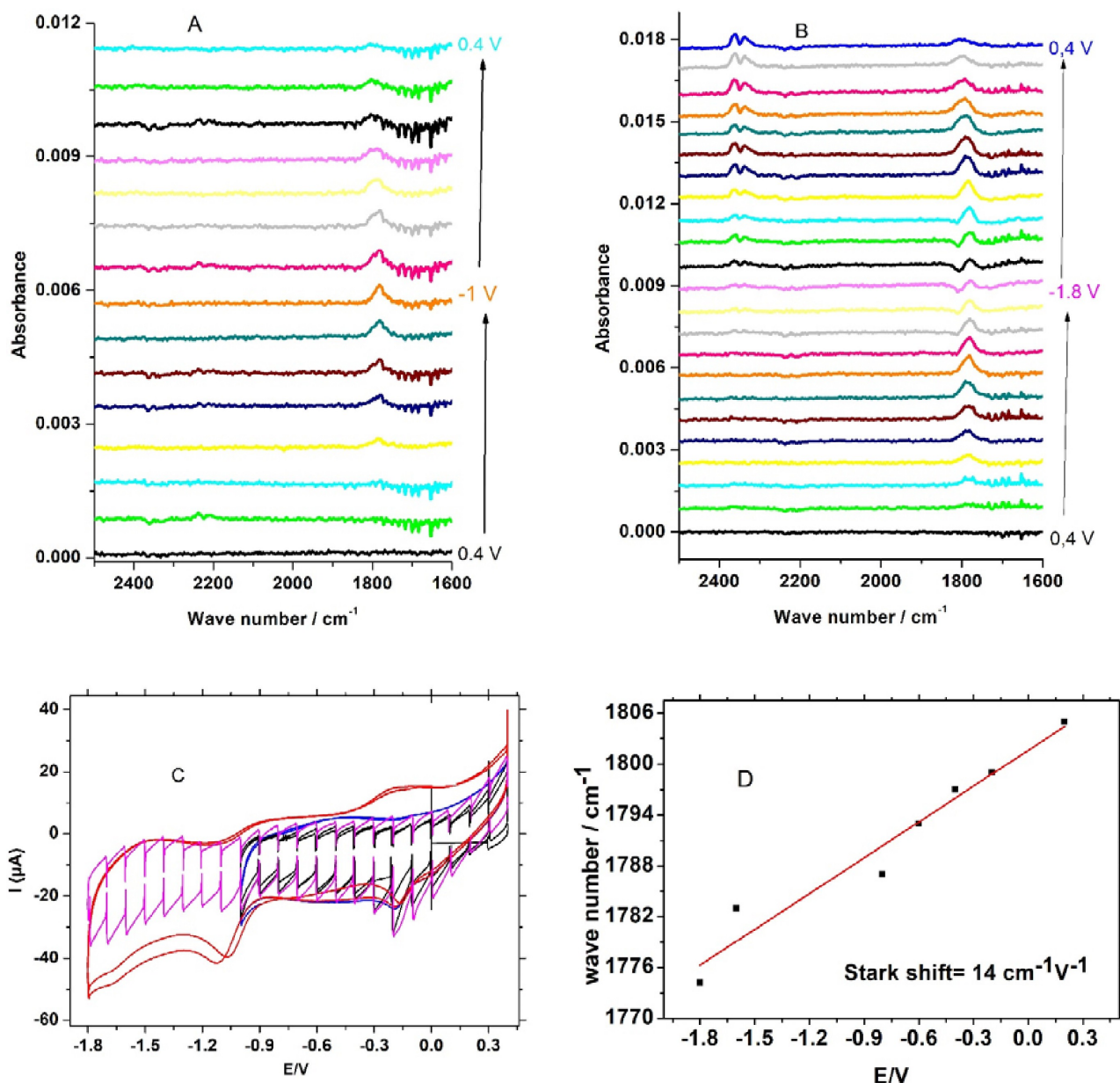


Figure 19. IR-spectra of propylene carbonate adsorbed on gold consisting of 32 interferograms with a resolution of 4 cm⁻¹. (A) IR-Spectra recorded in the potential limit from 0.4 to -1.0 V, (B) IR-Spectra recorded in the potential range from 0.4 to -1.80 V, (C) Corresponding CV. Electrolyte: 0.1 M KClO₄ in PC and (D) Shift of the wavenumber with the applied potential. The reference spectrum is collected at +0.4 V.

4. Conclusion

The interfacial double-layer structure on a gold single crystal and a roughened gold electrode in aprotic solvents has been investigated by using cyclic voltammetry and differential capacitance measurements. The most densely packed Au(111) face has a more positive zero charge potential (pzc) than the roughened Au(111) electrode; also, the differential capacitance at the pzc increases upon roughening. The pzc shifts to more positive potential and capacitance raises upon increasing water content from 1.28 to 58 mM on the roughened Au(111) electrode. The cation identity has no effect on the pzc. When we look at various solvents in interaction with the same metal

electrode and the salt, pzc vs. DMFc shifts as follows: ACN > DG > H₂O > PC > DMSO, and this order is not related to the dielectric properties of aprotic solvent, but this might be affected by the metal-solvent interaction and the donor number of the solvents. The pzc on the same electrode metal and solvent in different anions decreases in the order PF₆⁻ ≅ ClO₄⁻ > Br⁻.

Using a thermodynamic modelling framework, we could simulate the capacitance curves by only using the partial molar volume as variable – or, vice versa, we could determine the ion volume and thus the solvation number from the values of the capacitance maxima. The differing width of the capacitance minima could be qualitatively explained by a solvent layer

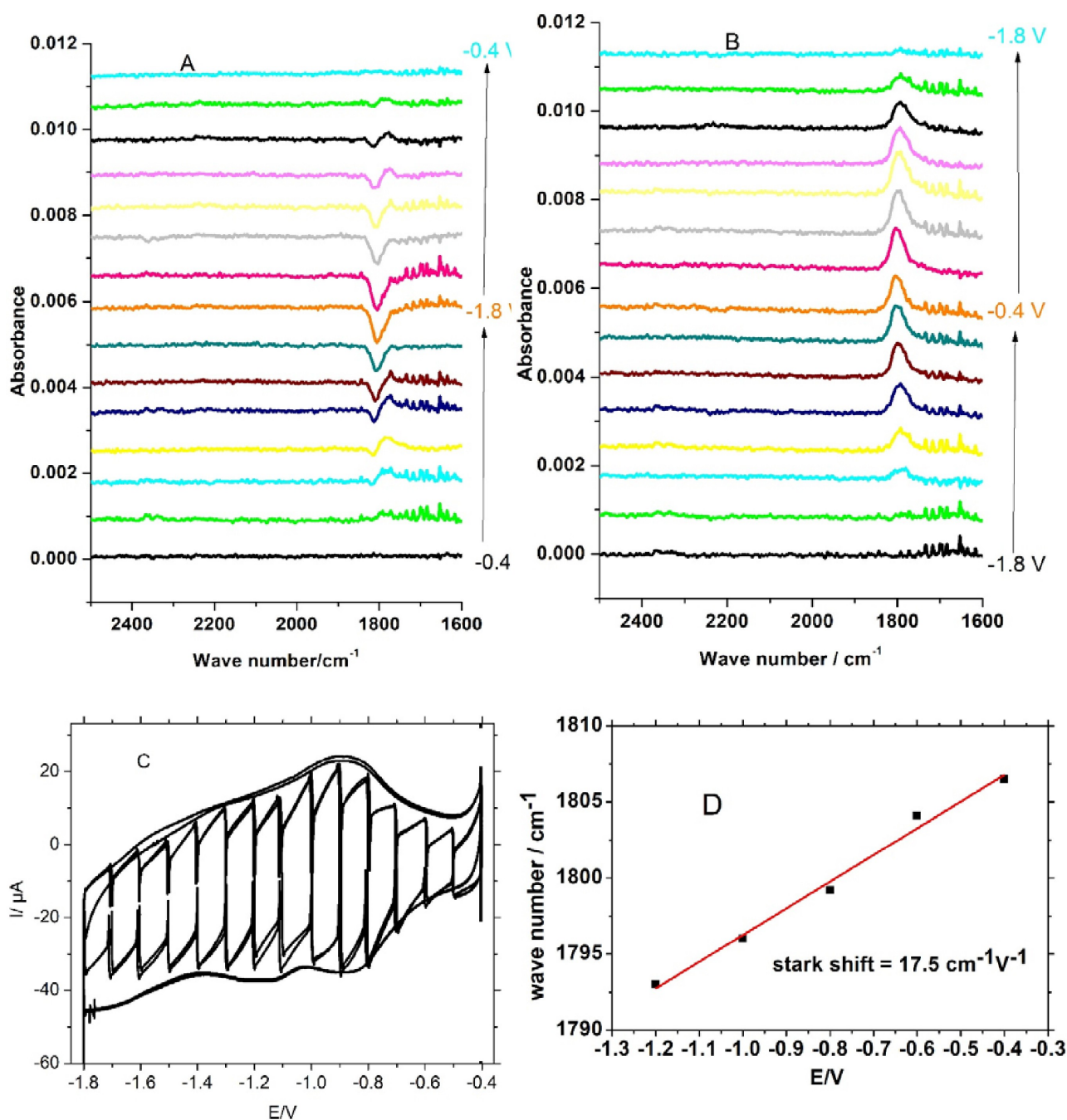


Figure 20. SEIRAS spectra recorded for Au thin film electrode in 10 mM KI + 0.1 M KClO₄/PC electrolyte at various reference potentials. (A) The reference potential was taken at -0.4 V, (B) It collected at -1.8 V, and (C) the corresponding CV at scan rate 10 mV/s and (D) Shift of the wavenumber with the applied potential.

attached to the electrode. This is only a first attempt in comparing capacitance data for nonaqueous electrolytes with theoretical modelling; in further work it will be advantageous to use silver electrodes since problems with surface reconstruction are avoided.

The presence of iodide in the electrolyte shifts the pzc to a more negative potential; consequently, at a given more positive potential, the electric field is stronger than in the absence of adsorbed iodide. This leads to a more substantial alignment of

PC molecules resulting in an intensity increase in our SEIRAS measurements. On the contrary, in absence of iodine, a stronger electrical field at low potentials leads to a more substantial alignment of the PC molecules and correspondingly to a higher absorbance.

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Conflict of Interest

The authors declare no conflict of interest.

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- [1] G. Valette, *J. Electroanal. Chem.* **1982**, 138, 37–54.
- [2] D. C. Grahame, *Chem. Rev.* **1947**, 41, 441–501.
- [3] Y. Hou, K. J. Aoki, J. Chen, T. Nishiumi, *J. Phys. Chem. C* **2014**, 118, 10153–10158.
- [4] M. M. Waeghele, C. M. Gunathunge, J. Li, X. Li, *J. Chem. Phys.* **2019**, 151, 160902.
- [5] A. S. Shatla, A. A. Abd-El-Latif, S. Ayata, D. Demir, H. Baltruschat, *Electrochim. Acta* **2020**, 334, 135556.
- [6] M. Arulepp, L. Permann, J. Leis, A. Perkson, K. Rumma, A. Jänes, E. Lust, *J. Power Sources* **2004**, 133, 320–328.
- [7] E. Lust, A. Janes, M. Arulepp, *J. Electroanal. Chem.* **2004**, 562, 33–42.
- [8] S. Trasatti, *J. Electroanal. Chem. Interfacial Electrochem.* **1971**, 33, 351–378.
- [9] G. Valette, *J. Electroanal. Chem.* **1982**, 139, 285–301.
- [10] A. N. Frumkin, O. A. Petrii, *Electrochim. Acta* **1975**, 20, 347–359.
- [11] S. Trasatti, E. Lust, in: *Modern Aspects of Electrochemistry*, Vol. 33 (Eds.: B. E. Conway, R. E. White, J. O. E. Bockris), Plenum Press, New York, **1999**.
- [12] S. Trasatti, *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, 150, 1–15.
- [13] S. Trasatti, *Mater. Chem. Phys.* **1985**, 12, 507–527.
- [14] A. Hamelin, Z. Vitanov, E. Sevastyanov, A. Popov, *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, 145, 225–264.
- [15] A. Hamelin, Z. Borkowska, J. Stafiej, *J. Electroanal. Chem. Interfacial Electrochem.* **1985**, 189, 85–97.
- [16] D. M. Kolb, J. Schneider, *Electrochim. Acta* **1986**, 31, 929–936.
- [17] J. Lipkowski, Z. C. Shi, A. C. Chen, B. Pettinger, C. Bilger, *Electrochim. Acta* **1998**, 43, 2875–2888.
- [18] G. Valette, *J. Electroanal. Chem.* **1989**, 269, 191–203.
- [19] G. Valette, *J. Electroanal. Chem.* **1989**, 260, 425–431.
- [20] G. Valette, *J. Electroanal. Chem.* **1987**, 224, 285–294.
- [21] G. Valette, A. Hamelin, R. Parsons, *Z. Phys. Chem.* **1978**, 113, 71–89.
- [22] G. Valette, A. Hamelin, *J. Electroanal. Chem.* **1973**, 45, 301–319.
- [23] R. Parsons, *Croat. Chem. Acta* **1980**, 53, 133–146.
- [24] G. Valette, R. Parsons, *J. Electroanal. Chem.* **1985**, 191, 377–386.
- [25] G. Valette, R. Parsons, *J. Electroanal. Chem.* **1986**, 204, 291–297.
- [26] U. W. Hamm, D. Kramer, R. S. Zhai, D. M. Kolb, *J. Electroanal. Chem.* **1996**, 414, 85–89.
- [27] A. Shen, J. E. Pemberton, *J. Electroanal. Chem.* **1999**, 479, 21–31.
- [28] C. N. Vanhuong, *J. Electroanal. Chem.* **1986**, 207, 235–246.
- [29] Z. Borkowska, A. Hamelin, *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, 241, 373–377.
- [30] M. Gnahn, T. Pajkossy, D. M. Kolb, *Electrochim. Acta* **2010**, 55, 6212–6217.
- [31] M. Gnahn, C. Muller, R. Repanszki, T. Pajkossy, D. M. Kolb, *Phys. Chem. Chem. Phys.* **2011**, 13, 11627–11633.
- [32] C. N. Vanhuong, *J. Electroanal. Chem.* **1985**, 194, 131–137.
- [33] G. Jarzabek, Z. Borkowska, *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, 226, 295–303.
- [34] Z. Borkowska, G. Jarzabek, *J. Electroanal. Chem.* **1993**, 353, 1–17.
- [35] E. Lust, in: *Encyclopedia of Electrochemistry* (Eds.: A. J. Bard, M. Stratman), Wiley, Weinheim, **2002**, pp. pp 188–224.
- [36] O. A. Petrii, I. G. Khomchenko, *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, 106, 277–286.
- [37] T. Biegler, R. Parsons, *J. Electroanal. Chem. Interfacial Electrochem.* **1969**, 22, A4–A6.
- [38] W. R. Fawcett, M. D. Mackey, *J. Chem. Soc., Faraday Trans. 1* **1973**, 69, 634–642.
- [39] Z. Borkowska, J. Stafiej, *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, 226, 283–293.
- [40] Z. Borkowska, *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, 244, 1–13.
- [41] R. Payne, *J. Am. Chem. Soc.* **1967**, 89, 489–496.
- [42] G. J. Hills, R. M. Reeves, *J. Electroanal. Chem. Interfacial Electrochem.* **1972**, 38, 1–15.
- [43] G. J. Hills, R. M. Reeves, *J. Electroanal. Chem. Interfacial Electrochem.* **1973**, 41, 213–230.
- [44] J. Taraszewska, *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, 121, 215–230.
- [45] V. V. Emets, B. B. Damaskin, *Russ. J. Electrochem.* **2009**, 45, 45–57.
- [46] V. V. Emets, B. B. Damaskin, *J. Electroanal. Chem.* **2000**, 491, 30–38.
- [47] M. D. Levi, A. V. Shlepakov, B. B. Damaskin, I. A. Bagotskaya, *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, 138, 1–27.
- [48] V. V. Emets, B. B. Damaskin, *J. Electroanal. Chem.* **2007**, 600, 191–204.
- [49] V. V. Emets, B. B. Damaskin, *Russ. J. Electrochem.* **2015**, 51, 789–795.
- [50] A. V. Shlepakov, I. A. Bagotskaya, *Sov. Electrochem.* **1982**, 18, 23–30.
- [51] I. A. Bagotskaya, C. N. Hay, V. G. Boitsov, V. E. Kazarinov, *Elektrokhimiya* **1988**, 24, 265–272.
- [52] A. N. Frumkin, N. B. Grigoryev, I. A. Bagotskaya, *Dokl. Akad. Nauk SSSR* **1964**, 157, 957–960.
- [53] I. A. Bagotskaya, V. V. Emets, V. G. Boytsov, V. E. Kazarinov, *Elektrokhimiya* **1988**, 24, 1145–1149.
- [54] V. V. Emets, A. A. Mel'nikov, *Russ. J. Electrochem.* **2018**, 54, 1012–1021.
- [55] S. Amokrane, Z. Borkowska, G. Jarzabek, *J. Electroanal. Chem.* **1994**, 377, 9–21.
- [56] M. Väärtou, E. Lust, *J. Electroanal. Chem.* **2014**, 733, 20–26.
- [57] M. Landstorfer, C. Guhlke, W. Dreyer, *Electrochim. Acta* **2016**, 201, 187–219.
- [58] W. Dreyer, C. Guhlke, R. Müller, *Phys. Chem. Chem. Phys.* **2013**, 15, 7075–7086.
- [59] W. Dreyer, C. Guhlke, M. Landstorfer, *Electrochem. Commun.* **2014**, 43, 75–78.
- [60] P. H. Reinsberg, H. Baltruschat, *Electrochim. Acta* **2020**, 334, 135609.
- [61] E. Lust, in: *Encyclopedia of Interfacial Chemistry* (Ed.: K. Wandelt), Elsevier, Oxford, **2018**, pp. 316–344.
- [62] Y. Liu, Y.-X. Yuan, X.-R. Wang, N. Zhang, M.-M. Xu, J.-L. Yao, R.-A. Gu, *J. Electroanal. Chem.* **2014**, 728, 10–17.
- [63] M. T. Alam, M. M. Islam, T. Okajima, T. Ohsaka, *J. Phys. Chem. C* **2008**, 112, 16600–16608.
- [64] M. T. Alam, M. M. Islam, T. Okajima, T. Ohsaka, *Electrochem. Commun.* **2007**, 9, 2370–2374.
- [65] I. Noviadri, K. N. Brown, D. S. Fleming, P. T. Gulyas, P. A. Lay, A. F. Masters, L. Phillips, *J. Phys. Chem. B* **1999**, 103, 6713–6722.
- [66] E. Mostafa, H. Baltruschat, *J. Solid State Electrochem.* **2013**, 17, 1861–1867.
- [67] V. D. Jovic, B. M. Jovic, *J. Electroanal. Chem.* **2003**, 541, 1–11.
- [68] W. Dreyer, C. Guhlke, R. Müller, *Entropy* **2018**, 20, 939.
- [69] S. R. De Groot, P. Mazur, *Non-equilibrium thermodynamics*, Dover Publications, New York, **1984**.
- [70] J. Meixner, *Ann. Phys.* **1943**, 435, 244–270.
- [71] M. Landstorfer, *Electrochem. Commun.* **2018**, 92, 56–59.
- [72] E. Panzram, H. Baumgärtel, B. Roelfs, C. Schröter, T. Solomun, *Ber. Bunsenges. Phys. Chem.* **1995**, 99, 827–837.
- [73] P. N. Ross, A. T. D'Agostino, *Electrochim. Acta* **1992**, 37, 615–623.
- [74] G. Gritzner, *J. Phys. Chem.* **1986**, 90, 5478–5485.
- [75] C. F. Riadigos, R. Iglesias, M. A. Rivas, T. P. Iglesias, *J. Chem. Thermodyn.* **2011**, 43, 275–283.
- [76] S. Y. Ha, Y. W. Lee, S. W. Woo, B. Koo, J. S. Kim, J. Cho, K. T. Lee, N. S. Choi, *ACS Appl. Mater. Interfaces* **2014**, 6, 4063–4073.
- [77] J. Applequist, J. R. Carl, K.-K. Fung, *J. Am. Chem. Soc.* **1972**, 94, 2952–2960.
- [78] W. M. Haynes, D. R. Lide, T. J. Bruno, *CRC Handbook of chemistry and physics*, 97th ed., CRC press, Boca raton, Florida, **2016**.
- [79] V. V. Pavlishchuk, A. W. Addison, *Inorg. Chim. Acta* **2000**, 298, 97–102.
- [80] V. J. Cunnane, G. Geblewicz, D. J. Schiffrin, *Electrochim. Acta* **1995**, 40, 3005–3014.
- [81] S. Trasatti, *Electrochim. Acta* **1987**, 32, 843–850.
- [82] S. Amokrane, J. P. Badiali, *J. Electroanal. Chem.* **1989**, 266, 21–35.
- [83] S. Amokrane, J. P. Badiali, *J. Electroanal. Chem.* **1991**, 297, 377–398.

- [84] S. Amokrane, *J. Electroanal. Chem.* **1993**, 361, 1–12.
- [85] G. Valette, *J. Electroanal. Chem.* **1981**, 122, 285–297.
- [86] A. Hamelin, J.-P. Bellier, *Surf. Sci.* **1978**, 78, 159–173.
- [87] D. Eberhardt, E. Santos, W. Schmickler, *J. Electroanal. Chem.* **1996**, 419, 23–31.
- [88] O. Oll, M. Väärtnou, G. Gorbatovski, J. Zhao, C. Siimenson, L. Siinor, K. Lust, T. Romann, P. Pikma, E. Lust, *Electrochim. Acta* **2019**, 319, 895–908.
- [89] A. S. Shatla, P. P. Bawol, H. Baltruschat, *ChemElectroChem* **2020**, 7, 4782–4793.
- [90] T. Langkau, H. Baltruschat, *Electrochim. Acta* **2002**, 47, 1595–1599.
- [91] M. Morita, M. Goto, Y. Matsuda, *J. Appl. Electrochem.* **1992**, 22, 901–908.
- [92] E. R. Nightingale, *J. Phys. Chem.* **1959**, 63, 1381–1387.
- [93] D. C. Grahame, *J. Electrochem. Soc.* **1951**, 98, 343.
- [94] A. Hamelin, L. Stoicoviciu, *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, 234, 93–105.
- [95] J. Friedl, I. I. E. Markovits, M. Herpich, G. Feng, A. A. Kornyshev, U. Stimming, *ChemElectroChem* **2017**, 4, 216–220.
- [96] S. Trasatti, in: *Advances in Electrochemistry and Electrochemical Engineering, Vol. 10* (Eds.: H. Gerischer, C. W. Tobias), Wiley, **1977**, pp. 213–321.
- [97] A. F. Silva, *Trends in interfacial electrochemistry, Vol. 179*, D. Reidel, Dordrecht, **1986**.
- [98] G. Valette, *J. Electroanal. Chem.* **1988**, 255, 215–224.
- [99] I. Hill, D. Irish, G. Atkinson, *Langmuir* **1986**, 2, 752–757.

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