Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2024, **34**, 85–87

Mendeleev Communications

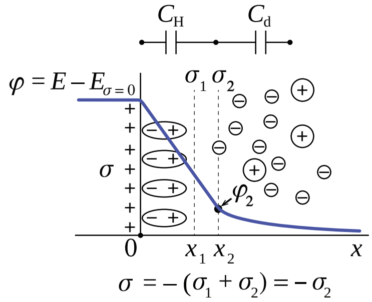
Electrical double layer at the interface of a Pb electrode with propylene carbonate solutions

Victor A. Safonov* and Maria A. Choba

Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation.
E-mail: safon@elch.chem.msu.ru, machoba@mail.ru

DOI: 10.1016/j.mencom.2024.01.025

The capacitance of the electrical double layer was measured *in situ* on a renewable Pb electrode in solutions of Bu_4NClO_4 in propylene carbonate (PC). The results and published data were analyzed using correlational relationships between the zero charge potentials ($E_{\sigma=0}$) of Hg, Pb, Sn, and Ga electrodes in solutions of surface-inactive electrolytes in PC, acetonitrile, and water on the one hand and the electron work functions of these metals (W_e) on the other hand. It was concluded that Pb electrodes interacted weakly with the molecules of these solvents.



Keywords: mechanically renewable Pb electrode, propylene carbonate, impedance method, surface-inactive electrolyte, electrical double layer (EDL), model description.

Nonaqueous solvents play an increasing role in practically important electrochemical processes, particularly, in modern electrochemical cells. Propylene carbonate (PC) is used in the electrolytes of lithium- and sodium-ion batteries and also in double-layer supercapacitors. The solvent mainly determines the structure of the electrical double layer (EDL), the adsorption of ions, and the kinetics of faradaic processes on the charged surfaces of metal and carbon materials. The interface between a carbon material in electrochemical cells and a nonaqueous electrolyte is complicated, and it depends on the method of synthesis and preliminary surface treatment of this material. It seemed interesting to study the EDL structure formed in such solutions on metal electrodes with surfaces well reproducible from one experiment to another.[1]

Note that electrochemical measurements on solid metal electrodes in nonaqueous solutions are a complicated experimental problem. Only few reliable data for such electrodes, *e.g.*, quantitative results for the individual faces of single crystals of Bi and other metals, were published.[2] This problem was solved using *in situ* measurements on electrodes with the surfaces renewed by cutting-off a thin metal layer immediately in solution without breaking the polarization circuit.[3–6] The mechanical renewal makes it possible to obtain reproducible surfaces free from oxides, other films, and uncontrolled impurities present in solution. Using this method, we obtained for the first time quantitative data on the interfaces formed by *s*, *p*, and *d* metals and alloys with different solutions including nonaqueous media.[7–9]

We used lead electrodes containing 99.999 at% Pb. The working electrode surface (the end surface of a wire 0.7 mm in diameter) was renewed by cutting off a thin metal layer (~10 μm) immediately in solution.[3–6] Solutions were prepared using anhydrous PC (99.7%, <0.002% water) and pure tetrabutylammonium perchlorate (TBAClO4) (both from Sigma-Aldrich). An aqueous saturated calomel electrode (S.C.E.) served as the reference electrode. The instruments and computer programs used for measuring and analyzing impedance spectra were described elsewhere.[5] Cyclic voltammograms measured in PC solutions of $TBAClO_4$ in a range from –1.85 to –0.25 V revealed the absence of pronounced current peaks due to faradaic processes. Based on an analysis of impedance diagrams, we found that, in the above range of potentials, the frequency dispersion of impedance components did not exceed 7–10% in the *f* interval from 100 to 2500 Hz. This allowed us to take the frequency *f* = 370 Hz as optimal when measuring the EDL capacitance. Thus, the above potential range can be considered (in good approximation) as the region of ideal polarizability of a Pb electrode in PC solutions.

Previously,[5] we analyzed the results obtained on a renewable Sn electrode in PC solutions of the surface-inactive electrolyte $TBAClO_4$ and concluded that PC dipoles interacted weakly with the surface of this metal. Here, we present new results on the measurements of EDL capacitance on a renewable Pb electrode in the above solutions. According to the literature, Pb is a promising component of various nanocomposite anodes in lithium- and sodium-ion batteries as an alternative to graphite and solid carbon materials with prospects of providing higher capacitance and higher energy density at a lower cost.[10,11] Lead was also considered as a dopant for cathodes with good performance characteristics.[12] Furthermore, a comparison of our data on the behavior of the Pb electrode in PC solutions with published data on the model electrodes of liquid *s*, *p* metals and alloys with ideally smooth (energy-homogeneous) surfaces[13–17] may be of fundamental science interest.

Figure 1(*a*) shows the dependences of differential capacitance on the potential measured on a Pb electrode in PC solutions of $TBAClO_4$ of different concentrations. The *C vs*. *E* dependences have a minimum at –0.61 ± 0.02 V with the depth increasing as the solution is depleted. Insofar as the potential of this minimum is almost independent of the electrolyte concentration, we can

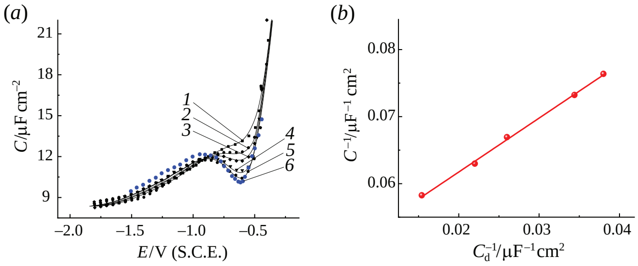


Figure 1 (*a*) *C vs. E* dependences (points) on the Pb electrode in PC solutions of $TBAClO_4$ at different concentrations, M: (*1*) 0.1, (*2*) 0.05, (*3*) 0.035, (*4*) 0.02, and (*5*) 0.016; (*6*) capacitance curve measured on a dropping Ga–Pb electrode in a 0.015 M solution of $LiBF_4$ in PC (according to Emets and Damaskin[17]). Solid lines show *C vs. E* dependences calculated using the Gouy–Chapman–Stern–Grahame model. (*b*) The Parsons–Zobel dependences[18] are plotted based on the data at $E_{\sigma=0}$.

infer the absence of specific adsorption of $TBAClO_4$ on the Pb surface. In other words, $TBAClO_4$ is a surface-inactive electrolyte and the capacitance minimum is associated with the maximum diffusivity of the EDL at a zero charge potential ($E_{\sigma=0}$).

The capacitance curves were analyzed within the framework of the classical model of EDL. Using the Parsons–Zobel method,[18] the $1/C$ *vs.* $1/C_d$ dependence was plotted, where C are the experimental capacitances in their minimum and C_d are the capacitances of the EDL diffuse part at $\sigma = 0$ calculated using the Gouy–Chapmen model for different electrolyte concentrations [Figure 1(*b*)]. The PC permittivity was assumed to be 64.4.[1] The slope of the linear dependence is reciprocal to the coefficient of surface roughness, which was found to be ~1.24. The linearity of the calculated dependence allowed us to conclude that the classical phenomenological Gouy–Chapmen–Stern–Grahame model of EDL can be applied to this system. Note that the extrapolation of this linear dependence to $1/C_d = 0$ (to an infinitely high electrolyte concentration) allows one to obtain the value of inner layer (or Helmholz layer) capacity, C_H, on the ordinate axis, which is assumed to be independent of the electrolyte concentration.

The applicability of the classical EDL model to our system was additionally confirmed by the capacitance curves [solid curves in Figure 1(*a*)] calculated by the Grahame method[19] for corresponding concentrations of $TBAClO_4$. They adequately coincided with the experimental dependences. Hence, no specific adsorption of $TBAClO_4$ from PC solutions on the Pb electrode surface was observed.

For comparison, Figure 1(*a*) shows the *C vs. E* dependence obtained on the electrode of a liquid Ga–Pb alloy (0.06 at% Pb) in the PC solution of $LiBF_4$ (according to Emets and Damaskin[17]). In this alloy, lead was a surface-active component, which was forced out to the surface layer. Hence, the dropping Ga–Pb electrode can be a model electrode with the ideally smooth energy-homogeneous surface, which imitates the properties of a liquid Pb electrode. The mechanical renewal procedure is analogous in a certain sense to the surface renewal procedure of dropping electrodes because it allows one to obtain the initial state of the electrode surface reproducible from one cut to another and free from uncontrollable impurities. At the same time, the freshly formed surface of a solid metal electrode (in contrast to a dropping liquid electrode) is not ideally smooth (as shown above, the roughness factor of a Pb electrode was ~1.24). Moreover, it cannot be called completely energy homogeneous. We believe that, because of this, the accuracy of such measurements on solid electrodes is somewhat lower, as compared with that of the precision measurements on model liquid alloy electrodes. As follows from Figure 1(*a*), our data obtained on the solid Pb electrode agree with the results obtained with a liquid Ga–Pb alloy electrode.

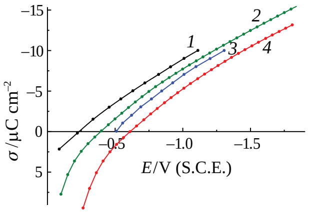


Figure 2 Dependences of σ on E for different electrodes in 0.1 M solutions of surface-inactive electrolytes in PC: (*1*) Hg,[16] (*2*) Sn,[5] (*3*) Ga,[16] and (*4*) Pb.

To assess the adsorption behavior of PC molecules on the Pb electrode, Figure 2 compares the dependence of the EDL charge density (σ) on the potential for the Pb electrode, which was calculated by integrating the *C vs. E* dependence in 0.1 M $TBAClO_4$, with an analogous dependence obtained earlier[5] for the renewable Sn electrode. Figure 2 also shows the σ *vs.* E curves measured in PC solutions on dropping Hg and Ga electrodes.[16] The shape of calculated σ *vs.* E dependences is similar for all electrodes shown here. In the potential interval corresponding to the high negative surface charges ($\sigma \leqslant -10$ μC cm^{-2}), these curves are almost parallel.

The shape of these dependences and the results of tentative calculations make it possible to conclude about the total absence or very weak specific interaction of these metals with PC molecules at high negative charges. However, at the potentials corresponding to the charges close to $\sigma = 0$ and also for $\sigma > 0$, the curves deviate from linearity due to an increase in the contribution made by the chemisorption interaction of the metal surface with PC molecules to the total potential drop at the interface. At the same time, this contribution (deviation from linearity) is small even for the Ga electrode (the most liophilic among mercury-like metals) in PC solutions, as compared with solvents such as dimethylformamide, dimethylsulfoxide,[20] and water.

To assess quantitatively the degree of liophilicity of the Pb electrode surface in contact with the PC solution, we considered correlations between the differences of the potentials of a metal M and mercury at $\sigma = 0$ and $\sigma = -10$ μC cm^{-2} ($\Delta E_{\sigma=0}^{\text{Hg–M}}$ and $\Delta E_{\sigma=-10}^{\text{Hg–M}}$) and differences between the work functions of this metal and mercury ($\Delta W_e^{\text{Hg–M}}$). Note that these correlations are based on concepts developed by A. N. Frumkin, which were analyzed in detail elsewhere.[21–23] According to these concepts, a linear relationship between the quantities $\Delta E_\sigma^{\text{Hg–M}}$ and $\Delta W_e^{\text{Hg–M}}$ is observed in the absence of chemisorption (non-Coulomb) interactions of a metal with solvent molecules. The deviation from linearity, which is usually observed in practice, suggests that the differences between the surface potential drops caused by adsorption of solvent molecules on mercury and the metal M ($\Delta\chi^{\text{S(Hg–M)}}$) and also between the surface potential drop formed in the metal phases of mercury and the metal M $\Delta(\delta\chi^{\text{Hg–M}})$ both contribute to $\Delta E_\sigma^{\text{Hg–M}}$.

Figure 3 compares $\Delta E_\sigma^{\text{Hg–M}}$ and $\Delta W_e^{\text{Hg–M}}/e$ for Hg, Pb, Ga, and Sn electrodes at $\sigma = 0$ and $\sigma = -10$ μC cm^{-2} in acetonitrile (AN), PC, and aqueous solutions of surface-inactive electrolytes. Dashed lines in Figures 3(*a*) and 3(*b*) correspond to the condition $\Delta E_\sigma^{\text{Hg–M}} = \Delta W_e^{\text{Hg–M}}/e$. The observed deviation of the potentials of different metals along the ordinate from the dashed line is associated with a chemisorption potential drop in these solvents. Figure 3(*a*) shows that, at $\sigma = 0$, the strongest chemisorption interaction was observed on the Ga electrode with water dipoles, whereas its interaction with AN and PC dipoles was much weaker. At $\sigma = 0$, the chemisorption interaction of Pb with solvent dipoles increased in the order AN < PC < H_2O. The same trend was observed on the Sn electrode.[5]

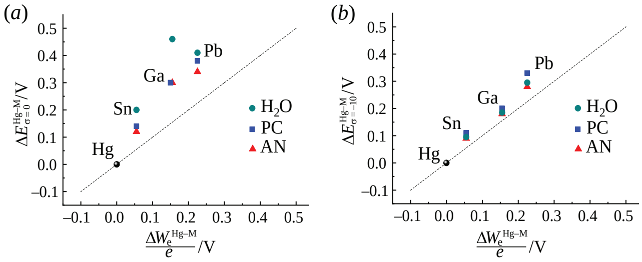


Figure 3 Comparison of $\Delta E_{\sigma}^{\text{Hg–M}}$ *vs.* $\Delta W_{e}^{\text{Hg–M}}/e$ dependences, where M is Hg,[16,20] Sn,[5] Pb, and Ga[16,20] at (*a*) $\sigma = 0$ and (*b*) $\sigma = -10$ μC cm^{-2} in AN, PC, and aqueous solutions of surface-inactive electrolytes. The values of W_e (4.25, 4.42, 4.32, and 4.475 eV for Pb, Sn, Ga, and Hg, respectively) were taken from handbook.[24]

Figure 3(*b*) shows that the deviation of the experimental values of $\Delta E_{\sigma=-10}^{\text{Hg–M}}$ from the dashed line is substantially smaller at $\sigma = -10$ than that at $\sigma = 0$ μC cm^{-2}. Thus, under these conditions, additional (as compared with $\Delta W_{e}^{\text{Hg–M}}$) contributions[21–23] to the potential difference $\Delta E_{\sigma}^{\text{Hg–M}}$, that is, the contributions primarily responsible for the chemisorption interactions of solvent molecules with metals, became considerably smaller (or/and were compensated).

Therefore, we can conclude that the interactions of Pb and Sn electrodes with PC, AN, and aqueous solutions are closely allied, and they can be assigned to lyophobic electrode systems. This conclusion for solid Pb and Sn electrodes well agrees with analogous conclusions[15–17,20,23] made on the basis of data on the EDL structure of liquid Ga–Pb and Ga–Sn electrodes in these solvents, and it can be considered as an evidence of its fundamental nature. In addition, the above results are of interest in the context of charge accumulation processes in supercapacitors and the use of lead as a component of electrodes for Li- and Na-ion batteries.

This work was supported by the Program of Development for the M. V. Lomonosov Moscow State University, topic no. AAAA-A21-121011590088-4.

References

1 *Nonaqueous Electrochemistry*, ed. D. Aurbach, Marcel Dekker, New York, 1999.
2 M. Väärtnõu and E. Lust, *J. Electroanal. Chem.*, 2022, **920**, 116618.
3 A. G. Zelinskii and R. Y. Bek, *Sov. Electrochem.*, 1985, **21**, 62 (*Elektrokhimiya*, 1985, **21**, 66).
4 V. A. Safonov, M. A. Choba and M. I. Buleev, *Russ. J. Electrochem.*, 2012, **48**, 163 (*Elektrokhimiya*, 2012, **48**, 181).
5 V. A. Safonov and M. A. Choba, *Mendeleev Commun.*, 2023, **33**, 726.
6 V. A. Safonov, M. A. Choba and M. S. Dolov, *J. Electroanal. Chem.*, 2020, **870**, 114174.
7 V. A. Safonov, M. A. Choba and O. A. Petrii, *J. Electroanal. Chem.*, 2018, **808**, 278.
8 V. A. Safonov, M. A. Choba and M. S. Dolov, *J. Electroanal. Chem.*, 2019, **851**, 13456.
9 V. A. Safonov and M. A. Choba, *J. Electroanal. Chem.*, 2022, **904**, 115951.
10 Q. Li, C. Xu, L. Yang, K. Pei, Y. Zhao, X. Liu and R. Che, *ACS Appl. Energy Mater.*, 2020, **3**, 7416.
11 Z. Chen, Y. Cao, J. Qian, X. Ai and H. Yang, *J. Solid State Electrochem.*, 2012, **16**, 291.
12 X. Zhang, Y. Xiong, M. Dong and Z. Hou, *J. Electrochem. Soc.*, 2019, **166**, A2960.
13 R. Payne, *J. Phys. Chem.*, 1967, **71**, 1548.
14 W. R. Fawcett and A. J. Motheo, *Electrochim. Acta*, 1991, **36**, 1971.
15 V. V. Emets, B. B. Damaskin and I. A. Bagotskaya, *Russ. J. Electrochem.*, 2001, **37**, 889 (*Elektrokhimiya*, 2001, **37**, 1038).
16 V. V. Emets, *Russ. J. Electrochem.*, 2001, **37**, 371 (*Elektrokhimiya*, 2001, **37**, 429).
17 V. V. Emets and B. B. Damaskin, *J. Electroanal. Chem.*, 2002, **528**, 57.
18 R. Parsons and F. G. K. Zobel, *J. Electroanal. Chem.*, 1965, **9**, 333.
19 D. Grahame, *Chem. Rev.*, 1947, **41**, 441.
20 V. V. Emets and B. B. Damaskin, *J. Electroanal. Chem.*, 2007, **600**, 191.
21 S. Trasatti and E. Lust, in *Modern Aspects of Electrochemistry*, eds. R. E. White, J. O'M. Bockris and B. E. Conway, Kluwer, New York, 1999, vol. 33, pp. 1–215.
22 B. B. Damaskin and V. A. Safonov, *Electrochim. Acta*, 1997, **42**, 737.
23 V. V. Emets and B. B. Damaskin, *Russ. J. Electrochem.*, 2009, **45**, 45 (*Elektrokhimiya*, 2009, **45**, 49).
24 *CRC Handbook of Chemistry and Physics*, 88th edn., ed. D. R. Lide, Taylor & Francis, Boca Raton, FL, 2007.

Received: 18th September 2023; Com. 23/7251