

# Adsorption of $\Gamma^-$ anions on Bi electrode from various solvents

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## ABSTRACT

In our recent works we studied the specific adsorption of  $\Gamma^-$  anions on Bi(111) single crystal electrode in some aprotic solvents to analyse the influence of the solvent on the adsorption process. The solvents used were those having important applications in electric double layer capacitors and batteries (acetonitrile, ethylene carbonate, propylene carbonate and gamma-butyrolactone). In the current paper we present a summary of our systematic work, showing the strong influence of the solvent on the adsorption characteristics of ions.

**KEYWORDS:** adsorption, iodide ion, bismuth, acetonitrile, ethylene carbonate, propylene carbonate, gamma-butyrolactone.

## 1. Introduction

The nature of the solvent has a remarkable influence on the electrical double layer structure, specific adsorption of ions and on the kinetics of various faradaic processes at the charged interfaces. Our work group has been studying the adsorption processes on electrodes from various solvents for a long time. Some of these nonaqueous solvents have an important and increasing role in applied electrochemistry, particularly in chemical power sources and energy storage devices such as batteries and electrical double layer capacitors (EDLLs) (see for example works [1-4]). In recent years, our studies on adsorption processes were concentrated on the solvents, applicable in EDLLs, namely ethylene carbonate (EC), propylene carbonate (PC), gamma-butyrolactone (GBL) and acetonitrile (AN).

We think that the influence of the solvent on the adsorption processes can most clearly be established using simple metal|electrolyte systems, where the methods of synthesis and pretreatment of the materials are less important than, for example, in the case of porous materials like carbon. In the present paper, we give a short review of the recent adsorption studies of  $\Gamma^-$  anions on the basal Bi(111) single crystal electrode from LiI solutions in PC [5], AN [6], GBL [7] and EC [8].

## 2. Methods of measurements and preliminary data

Bismuth is a suitable metal for double layer and adsorption studies because it is quite easy to get electrodes with smooth and reproducible surface, having a very wide region of ideal polarizability in many different solvents. Preliminary data for the characterization of the Bi|solution interface [5-8] were gathered by measuring the dependence of differential capacitance  $C$  on electrode potential  $E$  for the drop-like Bi electrode with melted surface [9] in solutions of surface-inactive electrolyte  $\text{LiClO}_4$ . The quantitative data and adsorption characteristics of  $\Gamma^-$  anions were obtained using the capacitance measurements at basal Bi(111) single crystal plane|solution interface, containing mixtures of LiI and  $\text{LiClO}_4$ . The preparation of this type of electrode has been described in [10]. The use of mixtures is necessary for applying the appropriate calculation method (Hurwitz-Parsons-Dutkiewicz method [11, 12]) for ionic adsorption parameters. For systems [5-8], reviewed in the present paper, the region of ideal polarizability is similar for all studied solvents and it is approximately from -1.6 to -0.3 V in the case of  $\text{LiClO}_4$  solutions and from -1.6 to -0.4 V for LiI solutions, measured against

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the aqueous saturated calomel electrode, connected with the cell through the ionic bridge. Impedance measurements were carried out using the Autolab PGSTAT 30 FRA 2 measurement system. Measurements were carried out at 25 °C, except for the EC system, where 40 °C was used. The high-grade purity LiI, LiClO<sub>4</sub> and solvents were used for the measurements without further purification [5-8]. Experimental details are more thoroughly described in our original studies [5-8].

In Figs. 1 and 2, the  $C,E$ -curves for Bi drop-like electrode in 0.1 and 0.01 M solutions in different solvents [5-8] are shown. For the sake of demonstrating the difference between protic and aprotic solvents, analogous curves for LiClO<sub>4</sub> solutions in ethanol [13] are also presented. As can be seen in Figs. 1 and 2, some differences exist in the  $C,E$ -curves: capacitance for EC and PC solutions is of similar value at cathodic potentials, but the sharper increase in  $C$  occurs in EC if  $E$  becomes less negative. At cathodic potentials, the increase in  $C$ , observed for ethanol [13] and AN [6], is practically absent in EC, PC and GBL, indicating that Li<sup>+</sup> cations are surface-inactive in these solvents. The  $C,E$ -curves in GBL differ from others to some extent: at cathodic potentials, the  $C$  values are lower than those in other aprotic solvents and the minimum potential, appearing in 0.01 M LiClO<sub>4</sub>, is about 0.05 V more positive than in other solvents.

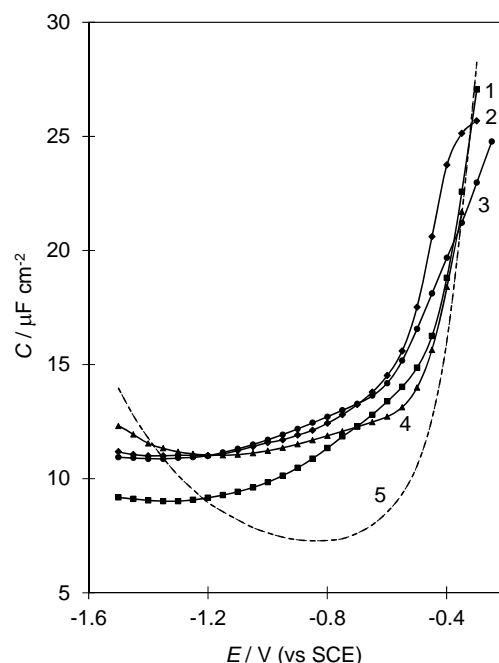
### 3. Methods of calculation of the charge of adsorbed ions and adsorption parameters

To get the surface excess of specifically adsorbed  $\Gamma$  ions, the  $C,E$ -curves for mixed solutions must first be integrated to find the electrode charge  $\sigma$  at each electrode potential and at fixed LiI concentration. Then, according to Hurwitz-Parsons-Dutkiewicz method [11, 12] the charge of specifically adsorbed ions  $\sigma_1$  can be calculated at constant  $\sigma$  or  $E$ , according to formulas

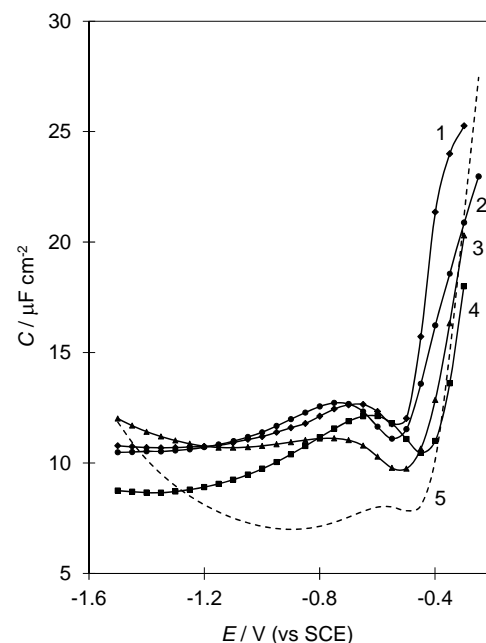
$$\sigma_1 = (F/RT)(\partial\Delta\xi / \partial \ln x)_{\sigma=\text{const}}, \quad (1)$$

$$\sigma_1 = (F/RT)(\partial\Delta\gamma / \partial \ln x)_{E=\text{const}}, \quad (2)$$

where  $\xi$  is the Parsons' function  $\xi = \gamma + \sigma E$  and  $\Delta\xi = \xi_0 - \xi$  at constant  $\sigma$ ,  $\gamma$  is the specific surface work value,  $\Delta\gamma = \gamma_0 - \gamma$  at constant  $E$  and the parameters with index <sub>0</sub> correspond to these values in the



**Fig. 1.** Differential capacitance curves (measured at 110 Hz) for the drop-like Bi electrode in 0.1 M LiClO<sub>4</sub> solutions in GBL (1), EC (2), PC (3), AN (4) and ethanol (5).



**Fig. 2.** Differential capacitance curves (measured at 110 Hz) for the drop-like Bi electrode in 0.01 M LiClO<sub>4</sub> solutions in EC (1), PC (2), AN (3), GBL (4) and ethanol (5).

supporting electrolyte. Coinciding  $\sigma_1$  values, calculated by both ways, gives an evidence of the self-consistency and correctness of the obtained data.

Next, the most important adsorption characteristic, the Gibbs energy of adsorption  $-\Delta G_A$ , was obtained by fitting the  $\sigma_1$  values to the semiempirical simple virial isotherm [5-8].

$$\ln [(\sigma_1/(zxc))] = -\Delta G_A/RT - 2\sigma_1/z, \quad (3)$$

where  $z$  is the charge number of adsorbed anion (-1 in the case of  $\Gamma$  anions),  $c$  is the total concentration of the solution (0.1 M) and  $B_{\text{eff}}$  is the second virial coefficient, characterising the mutual repulsion and size of the adsorbed ions. The  $B_{\text{eff}}$  is an effective parameter, because we have neglected the dependence of the diffuse layer potential drop  $\phi_2$  from  $\sigma_1$  in isotherm (3). However, the  $B_{\text{eff}}$  values can be used for qualitative comparison of the mutual interaction of adsorbed ions from various solvent systems [5-8, 13].

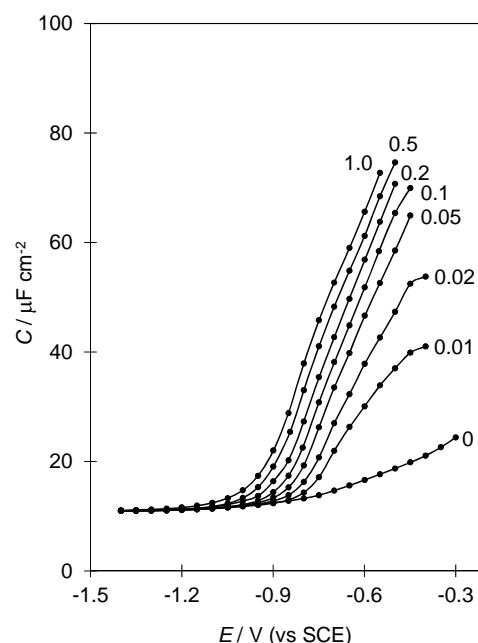
Another parameter, characterising the strength of adsorption of ions at electrode surface, the electrosorption valency (formal charge transfer coefficient)  $\gamma'$  [14, 15], can be calculated from the obtained adsorption data, according to the formula

$$\gamma' = -z(\partial\sigma/\partial\sigma_1)_E. \quad (4)$$

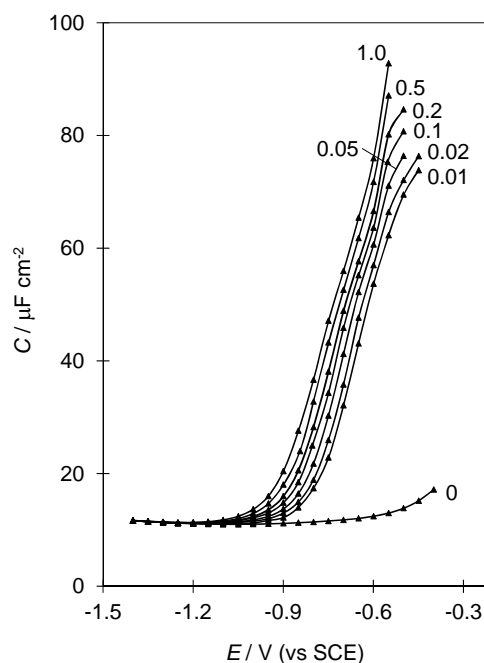
Although the  $\gamma'$  values are generally in correlation with the adsorption strength of ions in the same solvent at various electrodes and in some cases in different solvents at the same electrode, these values cannot be taken numerically equal to the real charge transfer value from ions to the electrode surface [16, 17].

#### 4. Adsorption of $\Gamma$ anions on Bi(111) single crystal plane electrode from various solvents

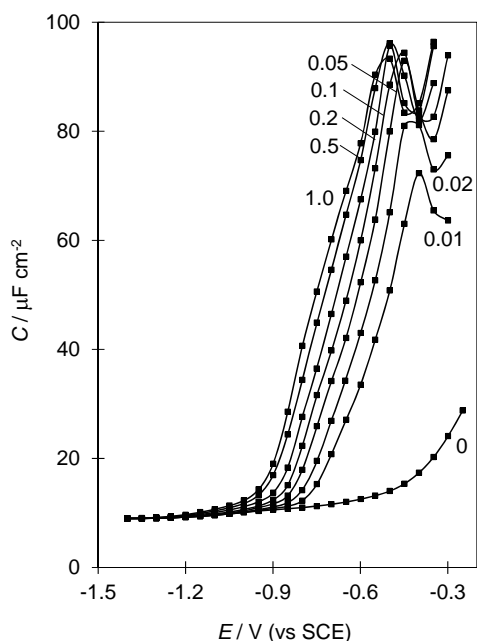
For calculation of charge of specific adsorption and adsorption characteristics in various solvents, the sets of  $C,E$ -curves in each solvent were measured [5-8]. The curves correspond to concentrations  $0.1x$  M LiI +  $0.1(1-x)$  M LiClO<sub>4</sub>, where  $x$  denotes the mole fraction of LiI in the mixture ( $0.01 \leq x \leq 1$ ; 9 solutions). These sets of  $C,E$ -curves for each solvent are presented in Figs. 3-6. The  $C$  values in these figures are the so-called low-frequency capacitance values, obtained by extrapolating the measured series capacitance  $C_s$  values to frequency  $f = 0$ . The maxima on  $C,E$ -curves at high LiI



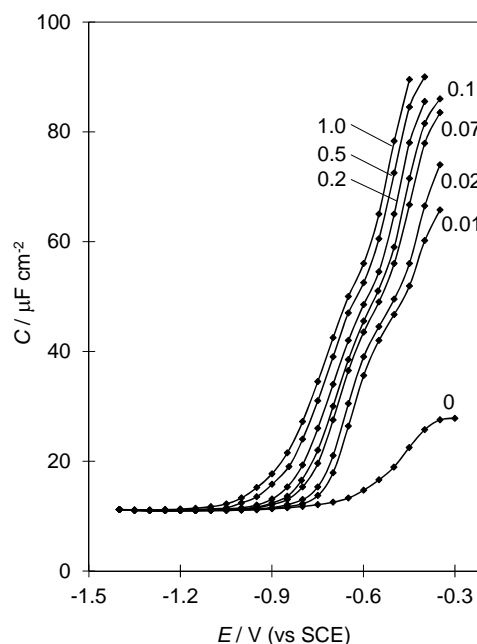
**Fig. 3.** Differential capacitance curves extrapolated to zero frequency for Bi(111) electrode in solutions  $0.1x$  M LiI +  $0.1(1-x)$  M LiClO<sub>4</sub> in PC. The values of  $x$  are given in the figure.



**Fig. 4.** Differential capacitance curves extrapolated to zero frequency for Bi(111) electrode in solutions  $0.1x$  M LiI +  $0.1(1-x)$  M LiClO<sub>4</sub> in AN. The values of  $x$  are given in the figure.



**Fig. 5.** Differential capacitance curves extrapolated to zero frequency for Bi(111) electrode in solutions 0.1x M LiI + 0.1(1-x) M LiClO<sub>4</sub> in GBL. The values of x are given in the figure.



**Fig. 6.** Differential capacitance curves extrapolated to zero frequency for Bi(111) electrode in solutions 0.1x M LiI + 0.1(1-x) M LiClO<sub>4</sub> in EC. The values of x are given in the figure.

**Table 1.** Potentials of zero charge ( $E_{\sigma=0}$ ) for the Bi(111) electrode in different solvents, measured in dilute solutions of LiClO<sub>4</sub>.

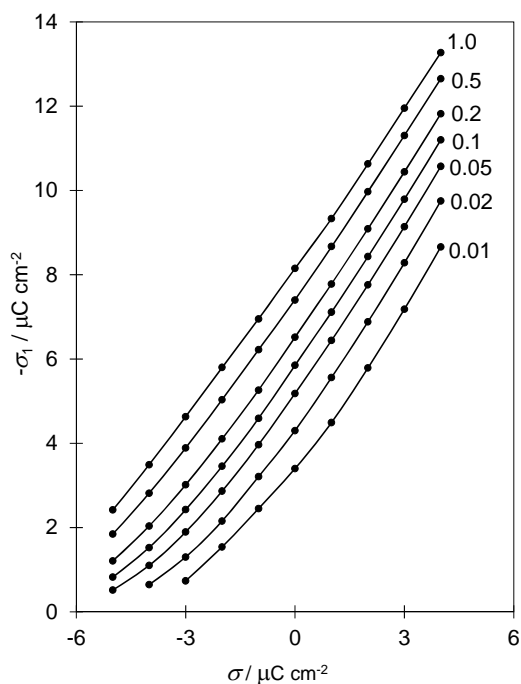
| Parameter          | EC [8]           | PC [5]           | GBL [7]          | AN [6]           |
|--------------------|------------------|------------------|------------------|------------------|
| $E_{\sigma=0}$ / V | $-0.47 \pm 0.01$ | $-0.50 \pm 0.02$ | $-0.44 \pm 0.01$ | $-0.50 \pm 0.01$ |

concentrations in the case of GBL (Fig. 5) are possibly caused by the change in the nature of adsorption bond between Bi(111) surface and I<sup>-</sup> ions (formation of surface compounds) when the surface charge of the electrode attains high positive values.

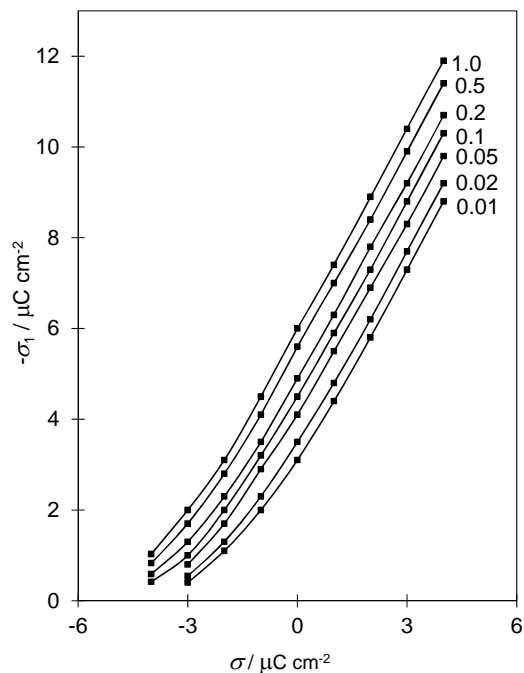
To calculate the electrode charge by integration of the  $C,E$ -curves, the potential of zero charge  $E_{\sigma=0}$  values for Bi(111) electrode in the studied solvents were obtained by potential value of the capacitance minimum, occurring at  $C,E$ -curves in dilute solutions (0.003 M LiClO<sub>4</sub> for studied solvents). These values are summarized in Table 1. It must be noted that because of the different liquid junction potentials between the working solution and reference electrode in different solvents, the obtained  $E_{\sigma=0}$  values can serve only as a beginning point of integration of  $C,E$ -curves and no other quantitative conclusions could be made.

After the integration, the  $\Delta\sigma$  and  $\Delta\zeta$  were calculated and Eqs. 1 and 2 were used for obtaining the charge of specifically adsorbed I<sup>-</sup> ions. Thus, the  $\sigma_1$  values were obtained for both  $\sigma$  and  $E$  as the independent electrical variable. The calculations were performed with the help of computer programs, written by us.

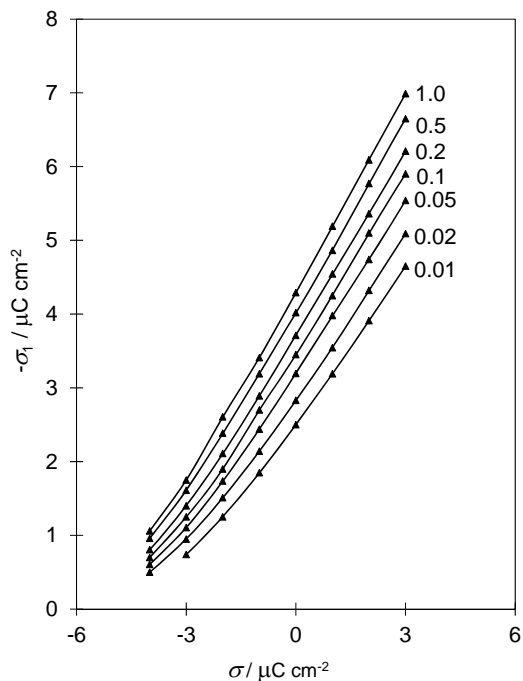
In Figs. 7-10, the  $\sigma_1,\sigma$ -curves for the adsorption of I<sup>-</sup> ions at various mole fractions of LiI in PC, GBL, AN and EC on the Bi(111) plane electrode are presented. The curves in Figs. 7-10 indicate that the strong adsorption of I<sup>-</sup> ions at the Bi|solution interface takes place from all solvents, but the dependences of  $\sigma_1$  on  $\sigma$ , and also on  $x$ , are somewhat different. In Figs. 11 and 12, the  $\sigma_1,E$ -curves at  $x = 1$  and  $x = 0.01$  are shown for different solvents. It follows from these figures that the  $\sigma_1$  values for GBL solutions are higher when



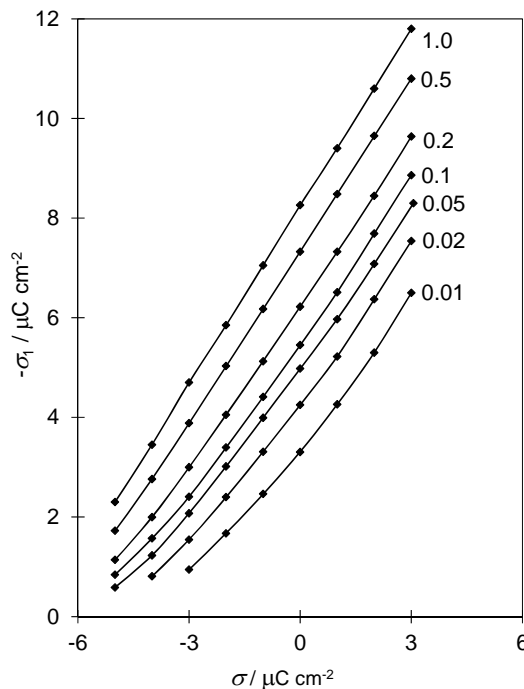
**Fig. 7.** Plots of the charge  $\sigma_1$  due to specifically adsorbed  $\Gamma$  anions against the electrode charge  $\sigma$  on Bi(111) electrode in PC for values of  $x$ , given in the figure.



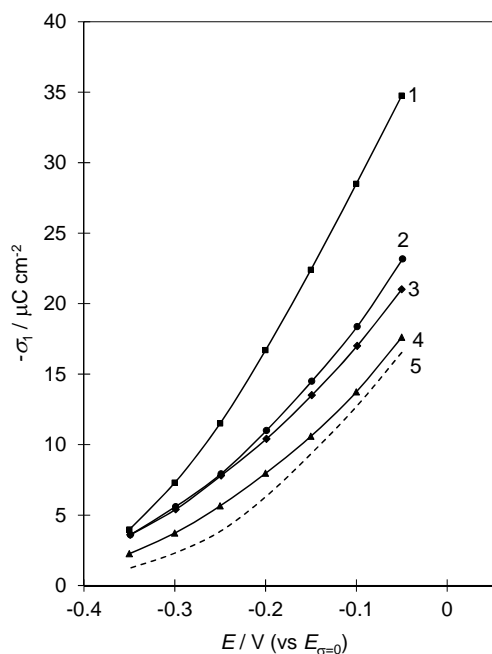
**Fig. 9.** Plots of the charge  $\sigma_1$  due to specifically adsorbed  $\Gamma$  anions against the electrode charge  $\sigma$  on Bi(111) electrode in GBL for values of  $x$ , given in the figure.



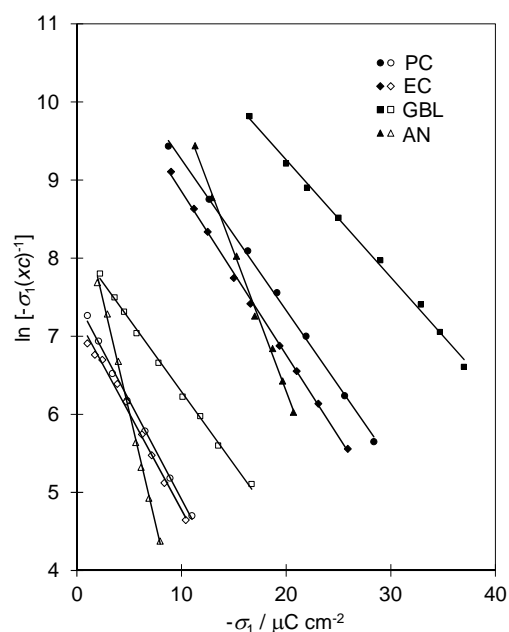
**Fig. 8.** Plots of the charge  $\sigma_1$  due to specifically adsorbed  $\Gamma$  anions against the electrode charge  $\sigma$  on Bi(111) electrode in AN for values of  $x$ , given in the figure.



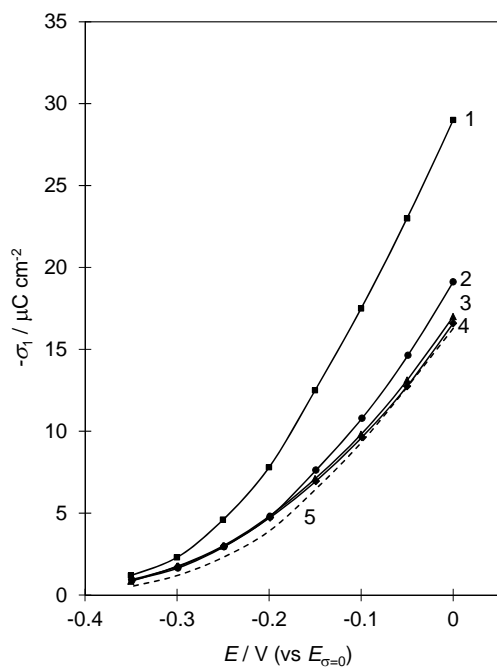
**Fig. 10.** Plots of the charge  $\sigma_1$  due to specifically adsorbed  $\Gamma$  anions against the electrode charge  $\sigma$  on Bi(111) electrode in EC for values of  $x$ , given in the figure.



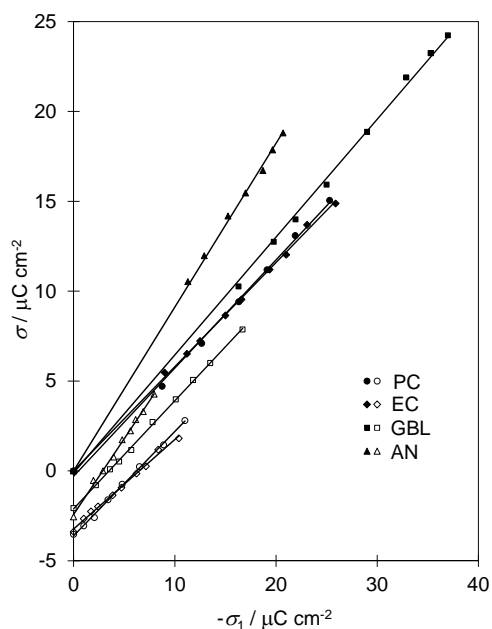
**Fig. 11.** Plots of the charge  $\sigma_1$  due to specifically adsorbed  $\Gamma$  anions against the electrode potential  $E$  on Bi(111) electrode at  $x = 1$  in GBL (1), PC (2), EC (3), AN (4) and ethanol (5).



**Fig. 13.** Plots of the function  $\ln[-\sigma_1/(xc)]$  against the charge  $\sigma_1$  of specifically adsorbed  $\Gamma$  anions at the Bi(111)|solution interface at electrode potential  $E/V$  (vs.  $E_{\sigma=0}$ ): filled markers - 0; empty markers - -0.2. The names of the solvents are given in the figure.



**Fig. 12.** Plots of the charge  $\sigma_1$  due to specifically adsorbed  $\Gamma$  anions against the electrode potential  $E$  on Bi(111) electrode at  $x = 0.1$  in GBL (1), PC (2), AN (3), EC (4) and ethanol (5).



**Fig. 14.** Plots of the electrode charge  $\sigma$  against the charge  $\sigma_1$  of specifically adsorbed  $\Gamma$  anions at the Bi(111)|solution interface at electrode potential  $E/V$  (vs.  $E_{\sigma=0}$ ): filled markers - 0; empty markers - -0.2. The names of the solvents are given in the figure.

**Table 2.** The values of standard Gibbs energy, second virial coefficient and formal charge transfer coefficient for adsorption of I<sup>-</sup> ions at the Bi(111) electrode from different solvents.

| Parameter                                       | Condition             | EC [8] | PC [5] | GBL [7] | AN [6] | Ethanol [13] |
|-------------------------------------------------|-----------------------|--------|--------|---------|--------|--------------|
| $-\Delta G_A^0 / \text{kJ mol}^{-1}$            | $E = E_{\sigma=0}$    | 100.6  | 101.5  | 104.2   | 104.7  | 99.2         |
|                                                 | $\sigma = 0$          | 100.0  | 102.0  | 103.9   | 105.1  | 98.5         |
| $B_{\text{eff}} / \text{nm}^2 \text{ ion}^{-1}$ | $E = E_{\sigma=0}$    | 1.6    | 1.6    | 1.5     | 3.7    | 2.1          |
|                                                 | $\sigma = 0$          | 6.4    | 7.2    | 10.4    | 15.2   | 11.2         |
| $\gamma'$                                       | $E \leq E_{\sigma=0}$ | 0.52   | 0.53   | 0.64    | 0.81   | 0.63         |

compared with other solvents and the difference in  $\sigma_1$  values diminishes at lower  $x$  values.

To get the adsorption parameters  $-\Delta G_A$ ,  $B_{\text{eff}}$  and  $\gamma'$ , the plots of  $\ln[\sigma_1/(zxc)]$  against  $\sigma_1$  at constant  $E$  and  $\sigma$  and  $\sigma$  against  $\sigma_1$  at constant  $E$ , were constructed and formulas (3) and (4) were applied [5-8]. These procedures are illustrated in Figs. 13 and 14. The results for different solvents are presented in Table 2. The  $-\Delta G_A^0$  values in Table 2 are  $-\Delta G_A$  values at common standard conditions for the virial isotherm (uncharged surface, 1 ion  $\text{cm}^{-2}$  on the electrode surface and 1 mol  $\text{dm}^{-3}$  of ions in the bulk of solution).

As can be seen in Table 2, the  $-\Delta G_A^0$  values at  $E = E_{\sigma=0}$  and  $\sigma = 0$  for one and the same solvent, may be considered as equal for each solvent studied, taking into account that differences in  $-\Delta G_A^0$  values are significant only when they are bigger than 1  $\text{kJ mol}^{-1}$  [5-8]. Looking at both  $-\Delta G_A^0$  and  $\gamma'$  values, it can be said that the adsorption activity of I<sup>-</sup> ions at Bi(111)|solution interface increases in the sequence of solvents ethanol < EC, PC < GBL < AN. However, it can also be seen that the  $B_{\text{eff}}$  values at both conditions for AN are much higher than those for other solvents. The high lateral repulsion of I<sup>-</sup> ions at Bi(111)|AN interface explains the low values of  $\sigma_1$  (Figs. 11 and 12) in spite of the high value of  $-\Delta G_A^0$ .

Finally, it must be remembered that the adsorption process on electrodes is not a simple metal-ion interaction, but also includes the metal-solvent and ion-solvent interactions. So, it must be kept in mind that  $-\Delta G_A^0$  in Table 2 is a complex parameter. The complexity of  $-\Delta G_A^0$  should be taken into

account if these values will be compared with some theoretical calculations in future.

## ACKNOWLEDGEMENTS

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## CONFLICT OF INTEREST STATEMENT

No conflicts.

## REFERENCES

- Conway, B. E. 1999, *Electrochemical Supercapacitors, Scientific Fundamentals and Technological Applications*, Kluwer Academic/Plenum, New York.
- Eikerling, M., Kornyshev, A. A. and Lust, E. 2005, *J. Electrochem. Soc.*, 152, E24.
- Tallo, I., Thomberg, T., Jänes, A., Kontturi, K. and Lust, E. 2012, *J. Electrochem. Soc.*, 159(3), A208.
- Väli, R., Laheäär, A., Jänes, A. and Lust, E. 2014, *Electrochim. Acta*, 121, 294.
- Väärtnõu, M. and Lust, E. 2012, *J. Electroanal. Chem.*, 686, 63.
- Väärtnõu, M. and Lust, E. 2014, *J. Solid State Electrochem.*, 18, 173.
- Väärtnõu, M. and Lust, E. 2014, *J. Electroanal. Chem.*, 733, 20.
- Väärtnõu, M. and Lust, E. 2017, *J. Solid State Electrochem.*, 21, 193.
- Damaskin, B., Palm, U., Petyäry, E. and Salve, M. 1973, *J. Electroanal. Chem.*, 47, 127.

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10. Lust, E. J. and Palm, U. V. 1985, *Sov. Electrochem.*, 21, 1186.
  11. Hurwitz, H. D. 1965, *J. Electroanal. Chem.*, 10, 35.
  12. Dutkiewicz, E. and Parsons, R. 1966, *J. Electroanal. Chem.*, 11, 100.
  13. Väärtnõu, M. and Lust, E. 2001, *Electrochim. Acta*, 47, 997.
  14. Vetter, K. J. and Schultze, J. W. 1972, *Ber. Bunsenges.*, 76, 927.
  15. Shi, Z. and Lipkowski, J. 1996, *J. Electroanal. Chem.*, 403, 225.
  16. de Levie, R. 2004, *J. Electroanal. Chem.*, 562, 273.
  17. Schmickler, W. and Guidelli, R. 2014, *Electrochim. Acta*, 127, 489.