

# Adsorption of iodide ions on the Cd(0001) single crystal plane in methanol

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**Abstract** The adsorption of  $I^-$  ions on the Cd(0001) single crystal plane from solutions in methanol has been investigated by impedance measurement method. The ionic charge due to the specific adsorption has been obtained using the mixed-electrolyte method for both electrode charge and electrode potential as the independent electrical variables. The Gibbs energy of adsorption of ions has been calculated using the different modifications of the virial adsorption isotherm. It was found that under comparable conditions, the results obtained at constant electrode potential and at constant electrode charge are coincident and the adsorption of  $I^-$  anion increases in the sequence of solvents: water < methanol, ethanol, and metals: Cd < Bi. The electrosorption valency has been calculated. It was found that on the Cd(0001) plane the electrosorption valency of  $I^-$  anions has a constant value that is similar for methanol and ethanol and also for these solvents on Bi single crystal planes.

**Keywords** Adsorption · Iodide ion · Cadmium · Methanol · Impedance

## Introduction

The specific adsorption of the halide ions on various metals has remarkable influence on the kinetics of various faradaic processes, including those having technological importance. In our earlier works, the adsorption of halide ions on Bi single crystal electrodes (Bi(hkl)) in water and

various alcohols have been extensively studied [1–5]. It was found that some adsorption and inner layer characteristics are substantially different in different solvents indicating the important role of the chemical nature of the solvent on the thermodynamic and kinetic data of the anion adsorption. Recently, the quantitative adsorption data of halide ions were obtained on Cd(0001) electrode in aqueous [6] and ethanolic [7, 8] solutions. Cd plays an important role in electrochemistry and energy technology; however, very few studies of adsorption of ions have been reported in the literature for single crystal cadmium electrodes [6–10], especially in nonaqueous electrolyte solutions. Therefore, it is of great interest, analogously to Bi electrode, to extend experimental studies into different solvents. Methanol was chosen for this investigation because this solvent has also technological importance, was used by us for the adsorption studies on Bi electrodes [3, 4] (therefore, the specific features of measurements in this solvent are well known), and it is of interest to find out how the nature of the alcohol influences the adsorption process parameters. The data obtained for Cd(0001)|water and Cd(0001)|ethanol interface showed that the adsorption of  $Br^-$  and especially  $Cl^-$  ions is quite weak at the potentials, where the measurements could be accomplished, and the quantitative data with high accuracy are, therefore, hard to obtain.

Thus,  $I^-$  anion was chosen to compare the adsorption in various media and the main aim of the present work is to obtain the quantitative characteristics of  $I^-$  anions adsorption on the electrochemically polished Cd(0001) plane in methanol using impedance measurement method. It was found that the region of electrode potentials,  $E$ , where the electrode can be considered as ideally polarisable is approximately the same in methanol and ethanol on the Cd(0001) electrode ( $-1.6 < E < -0.88$  V in the solutions of

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$\text{LiClO}_4$  and  $-1.6 < E < -0.95$  V in the solutions of LiI). Thus, data can be obtained only for uncharged and negatively charged electrode surface, because the potential of zero charge  $E_{\sigma=0}$  for Cd(0001) in methanol is close to positive end of the region of the ideal polarisability for Cd(0001) plane. However, the adsorption of  $\Gamma^-$  ions on Cd(0001) electrode from methanol is strong enough at these conditions to get reliable quantitative results.

## Experimental

The impedance data for Cd(0001) electrode in methanol in the present work were obtained using the Autolab PGSTAT 30 FRA 2 measurement system in the potential region  $-1.4 < E < -0.9$  V vs aqueous saturated calomel electrode (SCE), connected to the cell through a long salt bridge, containing 0.1 M solutions of  $\text{LiClO}_4$  in methanol and water. This construction is made for two reasons: first, to keep the liquid junction potential constant throughout the measurements and second, to avoid contamination of working solutions with chloride anions. It was found in our preliminary experiments that in this region of potentials in solutions, containing lithium salts ( $\text{LiClO}_4$ ,  $\text{LiCl}$ ,  $\text{LiBr}$ ,  $\text{LiI}$ ) in alcohols, no irreversible changes occur on the Cd electrode surface, and by cyclic voltammetry measurements, it was established that the current through the system did not exceed  $\pm 0.2$   $\mu\text{A}$ . At  $E > -0.88$  V, a sharp rise of anodic faradaic current was detected, indicating the oxidation process of Cd surface. However, in LiI solution, the increased dependence of measured capacitance from ac frequency was detected already at  $E = -0.93$  V.

For the adsorption studies, the series differential capacitance  $C$  of the Cd(0001) electrode was measured at several ac frequencies  $f$  in the range from 0.5 to 300 Hz. To use the traditional calculation methods, measurements were carried out in the mixed electrolyte solutions 0.1x M LiI + 0.1(1 - x) M  $\text{LiClO}_4$ , i.e. at the constant ionic strength where  $x$  denotes the mole fraction of LiI in the mixture ( $0.01 \leq x \leq 1$ ; 10 solutions) and  $\text{LiClO}_4$  is considered as a surface-inactive component. It was found earlier that the  $\text{ClO}_4^-$  ion undergoes a very weak specific adsorption on bismuth electrodes [11] only at positively charged surface from alcohols, but its activity is much less than of halide anions. As the adsorption data for Cd electrode can be obtained mainly at negative electrode charges and the adsorption of ions on Cd electrode is weaker than on Bi [6], the  $\text{ClO}_4^-$  ion should be suitable as indifferent electrolyte in the impedance measurements for cadmium electrode.

For calculation of the charge of specifically adsorbed ions  $\sigma_1$  in mixed electrolytes with the common counter ion, a comparatively simple and reliable Hurwitz–Parsons–Dutkiewicz method (proposed independently by Hurwitz

[12] and Dutkiewicz and Parsons [13]) is appropriate to use.

The high-grade purity LiI,  $\text{LiClO}_4$  (Aldrich) and methanol (Aldrich, 99.9%), were used for the measurements without further purification. Before measurement, all solutions were deaerated with ultrapure hydrogen from the hydrogen generator with Pd membrane.

The Cd single crystal electrodes were prepared according to the method described in [14], similarly for that of bismuth electrodes [15]. A massive Cd single crystal was grown by the horizontal Bridgeman method at the Institute of Problems of Microelectronics, Technology and Superpure Materials, Russian Academy of Science. Crystallographic orientation of Cd(0001) was determined using X-ray diffraction method using a special crystal holder and a goniometric head. The crystal was cut along the chosen orientation with a precision of  $\pm 0.3^\circ$ . The surface was polished to a mirror finish using standard metallographic procedure. The final surface diagram was recorded to determine the precise angle, and only those samples whose precision of orientation was better than  $\pm 0.15^\circ$  were used for electrochemical investigations. The final electrode surface preparation was obtained by electrochemical polishing in the aqueous  $\text{H}_3\text{PO}_4$  (Lachema, impurities less than 0.01 %) solution directly before measurements. Then the electrode was carefully rinsed with ultra purified (Millipore) water and methanol and cathodically polarised ( $-1.2$  V against SCE) in working solutions.

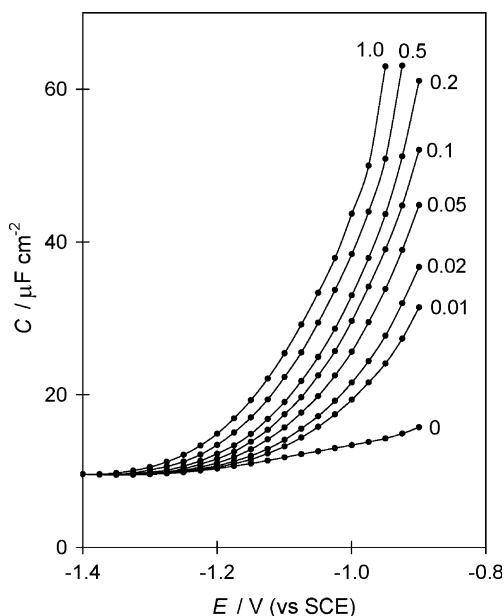
All other experimental details were similar to those for bismuth electrodes and are more thoroughly described in our previous studies [1–5].

## Results

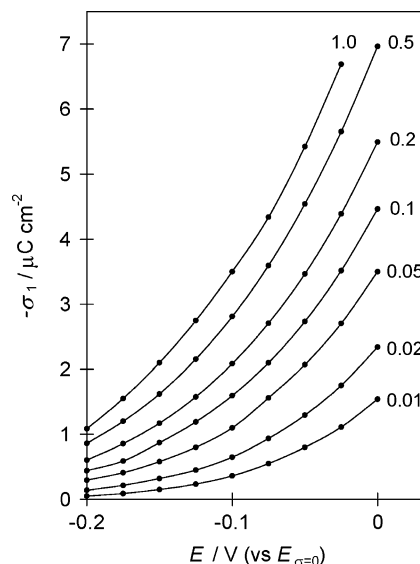
Similarly to Cd(0001) |  $\text{H}_2\text{O}$  [6], Cd(0001) | ethanol [7, 8] and Bi | alcohol [1–5, 16] systems the so-called low-frequency capacitance, obtained by extrapolating of the measured serial capacitance  $C_s$  values to frequency  $f=0$ , was used for the quantitative calculation of the charge of specifically adsorbed ions. Traditionally, the  $C_s - f^{1/2}$  plots are used for this purpose because these plots are usually linear in the wide range of lower frequencies (2–200 Hz for the present system, depending in some extent from  $E$  and composition of solutions). It was also found previously that in the case of Bi electrode, the charge values calculated from the low-frequency capacitance values are in a very good agreement with the data obtained directly by chronocoulometry for halide ions + alcohol | Bi(hkl) interface [3, 16]. It must be, however, noted that similarly to aqueous solutions [6] the frequency dependence of  $C_s$  in the mentioned frequency interval is quite weak. Additional calculations showed that if we use a single-frequency

capacitance (for example measured at 110 Hz), the obtained charge of specific adsorption differ very slightly from those values obtained from extrapolated low-frequency capacitance (difference is less than 5% at most values of  $E$  and mole fraction  $x$  of LiI studied). Similar results were obtained for Cd(0001) | ethanol systems [7, 8]. As in the solutions with the highest LiI concentrations ( $x=0.5$  and  $x=1$ ) the increased dependence of  $C$  from  $f$  was detected in the region of  $E$  from  $-0.93$  to  $-0.9$  V, and these data were excluded from the following calculations.

The  $C$ - $E$  curves for the system Cd(0001) |  $0.1x$  M LiI +  $0.1(1-x)$  M LiClO<sub>4</sub> in methanol are shown in Fig. 1 ( $x$  denotes the mole fraction of LiI). The rise of capacitance at  $E > -1.3$  V for solutions containing LiI indicates the strong adsorption of  $\Gamma^-$  ions on cadmium from methanol. The  $C$ - $E$  curves in the region where adsorption occurs are similar to those obtained by us for the Bi electrodes, except that the interval of  $E$ , where the capacitance was possible to measure is much narrower for Cd(0001) and the potentials, where capacitance maxima occur in the case of Bi [16], not reached for Cd(0001) in this experiment. The  $C$ - $E$  curve for LiClO<sub>4</sub> solution was integrated to establish the electrode charge  $\sigma$  using the potential of zero charge  $E_{\sigma=0}$  ( $-0.92 \pm 0.02$  V vs aqueous SCE, based on the diffuse layer minimum potential on  $C$ - $E$  curves in dilute solutions of LiClO<sub>4</sub> and LiBF<sub>4</sub> in methanol) as the starting point of the integration. For solutions containing iodide,  $\sigma$  values were obtained by back integration procedure [12, 13] from  $E = -1.4$  V, where the  $C$ - $E$  curves coincide and the adsorption of  $\Gamma^-$  is negligible. Further, the  $\Delta\sigma = \sigma_0 - \sigma$  values at constant  $E$



**Fig. 1** Differential capacitance curves for Cd(0001) electrode in solutions  $0.1x$  M LiI +  $0.1(1-x)$  M LiClO<sub>4</sub> in methanol for values of  $x$  given in the figure



**Fig. 2** Plot of the charge  $\sigma_1$  due to specifically adsorbed  $\Gamma^-$  anions against electrode potential  $E$  on Cd(0001) electrode for values of  $x$  given in the figure

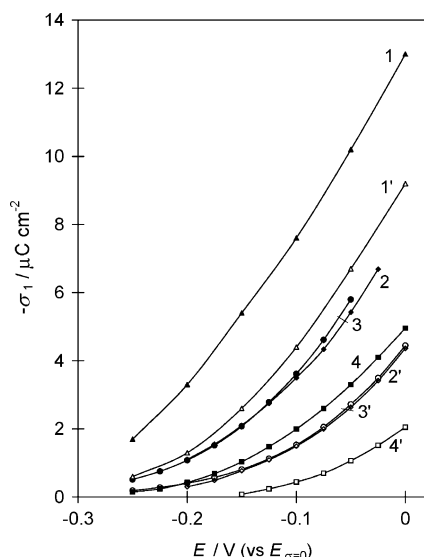
were calculated ( $\sigma_0$  is the  $\sigma$  value in  $0.1$  M LiClO<sub>4</sub> solution). Then by the integration of the  $\Delta\sigma$ - $E$  curves, the  $\Delta\gamma$ - $E$  curves were obtained, where  $\Delta\gamma = \gamma_0 - \gamma$ ,  $\gamma_0$  and  $\gamma$  are the specific surface work values in supporting electrolyte and in solutions containing  $\Gamma^-$ , respectively. After that, the values of Parsons' function  $\xi = \gamma + \sigma E$  and  $\Delta\xi = \xi_0 - \xi$  were calculated. The charge due to the specific adsorption of  $\Gamma^-$  ions  $\sigma_1$  was calculated according to the mixed electrolytes method [13] (Eqs. 1 and 2), for  $\sigma$  and  $E$  as the independent electrical variable

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

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

As was shown for Bi electrodes [4, 5], there are no reliable criteria which variable should be preferably chosen as the independent electrical variable. The following analysis was, therefore, performed for both cases. If the experimental data are correct the practically same  $\sigma_1$  values should be obtained at corresponding  $\sigma$  and  $E$  values. This condition was fulfilled for the present data similarly for Bi (hkl) electrodes [4, 5, 16].

In Fig. 2, the  $\sigma_1$ - $E$  curves for the adsorption of  $\Gamma^-$  ions at various concentrations of LiI in methanol on the Cd(0001) plane are given. In Fig. 3, the  $\sigma_1$ - $E$  curves at  $x=0.1$  and  $x=1$  are shown together with the analogous curves for Bi(111)| LiI + methanol [3], Cd(0001)| LiI + H<sub>2</sub>O [6] and Cd(0001)| LiI + ethanol [7] systems. As can be seen in Fig. 3, similarly to aqueous solutions [6],  $\sigma_1$  values for  $\Gamma^-$  at the Cd(0001) are lower than those for Bi(hkl) planes. From Fig. 3, it can also be concluded that the adsorption



**Fig. 3** Plot of the charge  $\sigma_1$  due to specifically adsorbed  $\Gamma^-$  anions against electrode potential  $E$  on Bi(111) (1, 1') and Cd(0001) (2–4, 2'–4') electrodes at  $x=1$  (1–4) and  $x=0.1$  (1'–4') in methanol (1, 1', 2, 2'), ethanol (3, 3') and water (4, 4')

activity increases significantly in the sequence of solvents: water < alcohols, but there is almost no difference between the results, obtained in methanol and ethanol.

## Discussion

To calculate the most significant characteristic of the adsorption of ions, the Gibbs energy of adsorption  $-\Delta G_A$ , the  $\sigma_1$  values should be fitted to an appropriate adsorption isotherm. For adsorption of ions, a physically justified isotherm is the virial isotherm taking into account the electrostatic work done to move the ion through the diffuse layer [17]

$$\ln(\sigma_1/zxc) + zF\phi_2/RT = -\Delta G_A/RT - 2B\sigma_1/z, \quad (3)$$

where  $z$  is the charge number of adsorbed anion ( $z=-1$  in the present case),  $\phi_2$  is the potential drop in the diffuse layer,  $c$  is the total concentration of solution (0.1 M) and  $B$  is the second virial coefficient, characterising the mutual repulsion and size of the adsorbed ion. As follows from Eq. 3, if the isotherm adequately describes the adsorption process, the plots of  $\ln(\sigma_1/zxc) + zF\phi_2/RT$  against  $\sigma_1$  should be linear. However, as was found in our previous studies for adsorption of inorganic anions at Bi(hkl) in non-aqueous solutions [ $c \geq 0.5$  M] or in the case where  $|\sigma + \sigma_1| \gg 0$ , i.e. if the adsorption is very weak or, on the contrary, at very strong adsorption. At the intermediate adsorption values ( $|\sigma| \approx |\sigma_1|$ ), that is the case for most studied systems [1–5, 16], the isotherm parameters could

not be obtained. On the other hand, it was found that for these systems [1–5, 16], the formally good description of adsorption data could be obtained using the semi-empirical simple virial isotherm

$$\ln(\sigma_1/zxc) = (-\Delta G_A)_{\text{eff}}/RT - 2B_{\text{eff}}\sigma_1/z, \quad (4)$$

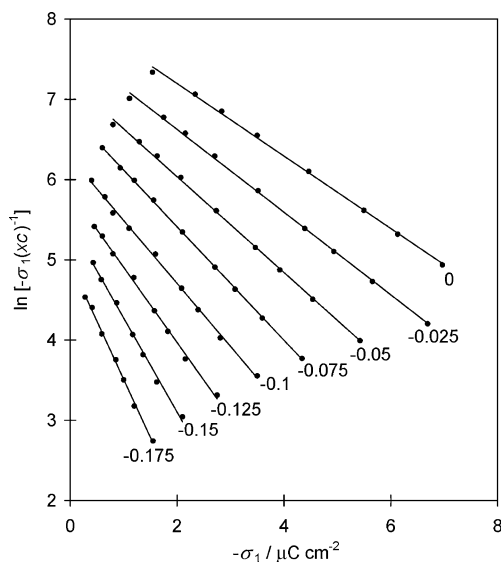
and the plots of  $\ln(\sigma_1/zxc)$  against  $\sigma_1$  for Bi(hkl) | nonaqueous ionic system were linear. The parameters in Eq. 4 are named  $(-\Delta G_A)_{\text{eff}}$  and  $B_{\text{eff}}$  to emphasise that their values have not explicit physical meaning and can only be used for qualitative comparison of interactions of adsorbed ions in different systems. It was shown in [2] that in the conditions  $\sigma_1 \rightarrow 0$ , the following dependencies exist between parameters of isotherms (3) and (4)

$$-\Delta G_A = (-\Delta G_A)_{\text{eff}} + zF\phi_2 \quad (5)$$

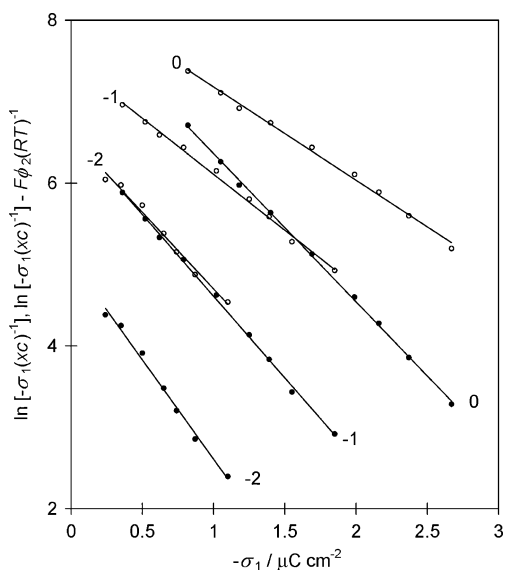
$$B = B_{\text{eff}} - (4A^2c + \sigma^2)^{-1/2}, \quad (6)$$

where  $A = (\varepsilon RT/2\pi)^{1/2}$ ,  $\varepsilon$  being the dielectric permittivity of the solvent.

It is important to notice that if we want to compare the  $\Delta G_A$  values in different systems, it is most appropriate to do it for uncharged electrode surface. So, we look at the quantity  $-\Delta G_A^0$  ( $-\Delta G_A$  at  $\sigma=0$  or at  $E = E_{\sigma=0}$ ) as determined for the conditions  $\sigma=0$  and  $\sigma_1 \rightarrow 0$ . In these conditions  $\phi_2 \rightarrow 0$  and isotherm (3) takes the form of isotherm (4). Thus, there should be no difference in  $-\Delta G_A^0$  values, obtained from these two isotherms. This result was experimentally proved in many systems for Bi | alcohol interface [2–5]. Consequently, in spite of semi-empirical



**Fig. 4** Plot of the function  $\ln(-\sigma_1/zxc)$  against the charge  $\sigma_1$  of specifically adsorbed  $\Gamma^-$  anions at the Cd(0001)/methanol interface at constant electrode potential. The electrode potential  $E/V$  (vs.  $E_{\sigma=0}$ ) is given in the figure



**Fig. 5** Plot of the functions  $\ln(-\sigma_1/xc)$  (filled circles) and  $\ln(-\sigma_1/xc) - F\phi_2/RT$  (open circles) against the charge  $\sigma_1$  of specifically adsorbed  $\Gamma^-$  anions at the Cd(0001)/methanol interface at constant electrode charge. The electrode charge  $\sigma/\mu\text{C cm}^{-2}$  is given in the figure

character of isotherm (4), the values of Gibbs adsorption energy, obtained for uncharged surface, correspond to real values and can be, therefore, used for further quantitative treatment.

The contradiction in the use of various modifications of virial isotherm (better results for physically less justified isotherm) was comprehensively analysed in our previous study [2]. It was proposed that the traditional method of calculation of  $\varphi_2$  potential in the presence of adsorbed ions by simply changing  $\sigma$  with  $\sigma + \sigma_1$  in the Gouy–Chapman theory is probably not justified. As a possible reason for that, the concept of ion-pairing in the inner part of double layer was proposed. The last explanation, however, was not totally accepted [18]. Nevertheless, no better explanation could be found in later studies.

Therefore, in the present study isotherm (4) is appropriate for the calculation of the adsorption parameters. However, in the present system the condition  $|\sigma + \sigma_1| \gg 0$

is fulfilled at  $\sigma = \text{const}$  (but not at  $E = \text{const}$ ) and then, as explained above, isotherm (3) also formally describes the adsorption of ions. Thus, at  $\sigma = \text{const}$ , the calculation of the adsorption parameters is possible for both isotherms. In Fig. 4, the plots corresponding to Eq. 4 for Cd(0001) |  $\Gamma^-$  interface in methanol at  $E = \text{const}$  are presented. In Fig. 5, the plots corresponding to both Eqs. 3 and 4 for Cd(0001) |  $\Gamma^-$  interface in methanol at  $\sigma = \text{const}$  are presented. As can be seen from Figs. 4 and 5, the linear plots are obtained in all cases. The correlation coefficients for plots corresponding to Eq. 3 were found to be between 0.993 and 0.999 and for Eq. 4 from 0.987 to 0.995. This permits to calculate the adsorption parameters of  $\Gamma^-$  anions at Cd(0001) | methanol interface. As was expected, no linear plots were obtained at  $E = \text{const}$  for isotherm (3).

According to Eqs. 3 and 4, the extrapolation of the straight lines in Figs. 4 and 5 to the condition  $\sigma_1 = 0$  yields to  $-\Delta G_A$  for given electrode potential or charge. The  $-\Delta G_A$  values were calculated using the common standard conditions for the virial isotherm (1 ion  $\text{cm}^{-2}$  on the electrode surface and 1 mol  $\text{dm}^{-3}$  of ions in the bulk of solution). The  $-\Delta G_A - E$  plots for the present system were found to be nearly linear but because of narrow range of  $E$  (or  $\sigma$ ), where the data is possible to obtain (and the very low values of  $\sigma_1$  at lower  $E$  (Fig. 2)), it must be taken only as a first approximation. The  $-\Delta G_A^0$  values ( $-\Delta G_A$  at  $\sigma = 0$  or  $E = E_{\sigma=0}$ ) for the adsorption of  $\Gamma^-$  ions for various modifications of isotherm and independent electrical variables are presented in Table 1. As it was shown in [2] and mentioned above,  $-\Delta G_A^0$  is a good characteristic for the comparison of the adsorption of ions in various solvents and on various surfaces because this value is independent from electrolyte concentration  $c$  at  $E = E_{\sigma=0}$  or  $\sigma = 0$  and the  $-\Delta G_A^0$  values should be the same for different modifications of virial isotherm.

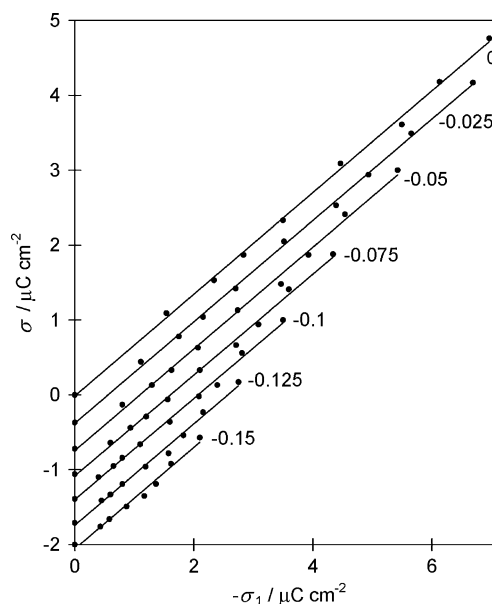
As can be seen from Table 1, the calculated  $-\Delta G_A^0$  values are indeed very close for different isotherms and electrical variables and can be taken as equal in the limits of precision. For the sake of comparison, in Table 1, alongside with the adsorption parameters for  $\Gamma^-$  anions at the Cd(0001) plane in methanol, the same adsorption parameters for  $\Gamma^-$  anions at the Cd(0001) plane in aqueous

**Table 1** The values of standard Gibbs energy and virial coefficient in virial isotherms for adsorption of  $\Gamma^-$  ions on the Cd(0001) electrode in methanol and on other interfaces [4, 6, 7]

Parameter	Condition	Cd(0001) methanol	Cd(0001) ethanol	Cd(0001) water	Bi(111) methanol
$-\Delta G_A^0/\text{kJmol}^{-1}$ (Eq. 3)	$\sigma = 0$	94.0	94.7	–	–
$-\Delta G_A^0/\text{kJmol}^{-1}$ (Eq. 4)	$E = E_{\sigma=0}$	93.5	94.3	–	95.2
	$\sigma = 0$	93.8	94.5	88.6	94.2
$B_{\text{eff}}/\text{nm}^2 \text{ ion}^{-1}$	$E = E_{\sigma=0}$	3.6	4.1	–	–
	$\sigma = 0$	14.4	16.0	–	13.5
$B/\text{nm}^2 \text{ ion}^{-1}$	$\sigma = 0$	11.2	10.1	5.0	–

[6] and ethanolic [7] solutions and for  $\Gamma^-$  anions at the Bi(111) planes in methanol [3, 4] are presented. If we compare the  $-\Delta G_A^0$  values for  $\Gamma^-$  anion adsorption at various metals and in various solvents, we should remember that  $\Delta G_A$  consists of contributions of the energies of various interactions. In the case of adsorption of ions, it is usually stated that  $\Delta G_A = \Delta G_{M-A} + \Delta G_{M-S} + \Delta G_{S-A}$ , where the components of  $\Delta G_A$  are the energies of corresponding interactions (M—metal, A—anion, S—solvent). It is seen from Table 1 that at the Cd(0001) electrode the  $-\Delta G_A^0$  values for  $\Gamma^-$  anion in methanol and ethanol are quite close but are significantly higher than the  $-\Delta G_A^0$  value for  $\Gamma^-$  anion in water. It indicates that water molecules are either more strongly adsorbed on Cd(0001) surface than alcohol molecules or are  $\Gamma^-$  anions more strongly solvated in water. Most possibly, the both reasons should be taken into account. It is interesting to note that in methanol, there is quite little difference in  $-\Delta G_A^0$  values between Cd and Bi electrodes. In ethanol, however, more significant difference was found [7]. In other words, on the Cd(0001) electrode, the adsorption characteristics for  $\Gamma^-$  ions in various alcohols depend much less on alcohol chemical composition than on Bi(hkl) electrodes. It shows a somewhat different character of metal–solvent interaction on these two metals.

It should be noted that the units of virial coefficient  $B$  values, obtained from Eqs. 3 and 4, are  $\text{cm}^2 \mu\text{C}^{-1}$ . However, traditionally, these values are presented as  $\text{nm}^2 \text{ion}^{-1}$  (the transition coefficient being 16). So, in the Table 1, the  $B$  and  $B_{\text{eff}}$  values are presented in  $\text{nm}^2 \text{ion}^{-1}$ , analogously to our previous works. It is also possible to compare the  $B$  values, estimated from Fig. 5 and calculated by Eq. 6 from  $B_{\text{eff}}$ . For  $\sigma=0$ , the calculated value is  $10.6 \text{ nm}^2 \text{ion}^{-1}$ , in satisfactory agreement with the value in Table 1. As can be seen from Table 1, the second virial coefficient  $B$  values for  $\Gamma^-$  ions on Cd(0001) electrode are slightly higher than the  $B$  values of Bi electrode. At the same time, the  $B$  value for  $\Gamma^-$  anion adsorption similarly to ethanol, studied in [7], from methanol is significantly higher than the  $B$  value for aqueous solutions. It is a predictable result, because the distance of outer Helmholtz plane from electrode surface  $x_2$  in non-aqueous media is probably bigger than in water and, as was shown in work [19], the parameter  $B$  is connected with  $x_2$  by the integral capacitance between inner and outer Helmholtz planes  $K_{12}$  ( $K_{12} = K_{02}x_2/(x_2 - x_1)$ ), where  $K_{02}$  is the integral capacitance of the inner part of the double layer and  $x_1$  is the



**Fig. 6** Plot of the electrode charge  $\sigma$  against the charge  $\sigma_1$  of specifically adsorbed  $\Gamma^-$  anions at the Cd(0001)/methanol interface. The electrode potential  $E/V$  (vs.  $E_{\sigma=0}$ ) is given in the figure

distance of inner Helmholtz plane from electrode surface.

$$B = \lambda F / RTK_{12}, \quad (7)$$

where  $\lambda$  is the so-called ratio between micropotential and macropotential.

Another parameter characterising the adsorption process of ions is the so-called electrosorption valency (formal charge transfer coefficient)  $\gamma'$  [20]. The  $\gamma'$  values can be calculated according to the formula [21]

$$\gamma' = (1/F)(\partial \Delta G_A / \partial E)_\Gamma = -(1/F)(\partial \sigma / \partial \Gamma)_E, \quad (8)$$

where  $\Gamma$  is the surface excess of adsorbed ions ( $\Gamma = \sigma_1 / zF$ ). Following Eq. 8, there are two ways of calculating  $\gamma'$ . However, taking into account the narrow interval of  $E$  where  $-\Delta G_A - E$  plot can be constructed in the present case, the use of the second possibility (from the slope of the  $\sigma - \Gamma$  or  $\sigma - \sigma_1$  plot) was considered more appropriate. So, the  $\sigma - \sigma_1$  plots at constant  $E$  were constructed (given in Fig. 6). As can be seen from Fig. 6, the  $\sigma - \sigma_1$  plots for the adsorption of  $\Gamma^-$  ions on Cd(0001) plane in a good approximation may be considered as linear and nearly parallel lines. Analogous plots in methanol were obtained for Bi(111) plane, but for other Bi planes, the lines were not parallel [4]. The parallelism of lines in Fig. 6 shows the

**Table 2** The formal charge transfer coefficient for  $\Gamma^-$  ions adsorbed on the Cd(0001) electrode in methanol and on other interfaces [4, 6, 7] at  $E \leq E_{\sigma=0}$

Parameter	Cd(0001) methanol	Cd(0001) ethanol	Cd(0001) water	Bi(111) methanol
$\gamma'$	0.68	0.72	0.51	0.69

constancy of  $\gamma'$  at  $\sigma \leq 0$  in the present system under study. The values of  $\gamma'$  are presented in Table 2. As in Table 1, the comparable parameters for Cd(0001)|water [6] and Bi(hkl)|methanol [5] interfaces are also included. As follows from Table 2,  $\gamma'$  values are close for different metals and single crystal planes but are to some extent higher in methanol than in water, reflecting the different structure of the double layer in aqueous and non-aqueous media.

## Conclusion

The impedance and cyclic voltammetry measurements indicated that the Cd(0001) single crystal plane in LiClO<sub>4</sub> and LiI solutions in methanol is stable in the interval of potentials at least from  $-1.6$  to  $-0.88$  V (vs aqueous SCE). At  $E > -0.88$  V (SCE), the rapid increase of anodic faradaic current was detected. The interval of potentials where the adsorption characteristics of the  $\Gamma^-$  ions in methanol on the Cd(0001) plane have been obtained, using the traditional calculation methods, was from  $-1.4$  to  $-0.9$  V in solutions with mole fraction of LiI less than 0.5 and  $-1.4 \leq E \leq -0.93$  V with higher LiI content.

It was found that the choice of electrical variable used did not had effect on the charges of specifically adsorbed  $\Gamma^-$  anions obtained on the Cd(0001) single crystal plane in the LiI solutions, indicating that there were no significant systematic errors in obtaining and handling of the experimental data. It was also found that the adsorption of  $\Gamma^-$  anions from methanol decreases in the sequence of electrodes Bi(hkl) > Cd(0001). The value of the standard Gibbs energy of adsorption of  $\Gamma^-$  anions is also slightly lower for Cd(0001) electrode than that for the Bi(hkl) electrodes, indicating that the  $\Gamma^-$  anions interact more strongly with the bismuth electrode and/or the solvent molecules are more strongly adsorbed on Cd(0001) plane. It was found that mutual repulsion of adsorbed anions and the structure of the metal | solution interface are also essential factors in determining the extent of the adsorption. The adsorption of  $\Gamma^-$  anions as well as the Gibbs

energy of adsorption on the Cd(0001) single crystal plane are close in methanol and ethanol, but these values are significantly higher if compared with water, reflecting the decreasing of the metal–solvent and ion–solvent interactions in non-aqueous media. The electrosorption valency obtained for the  $\Gamma^-$  ion was found to be somewhat higher in methanol and ethanol than in water but almost independent of the metal studied.

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