

Study of adsorption of tetraethylammonium ions on Bi single crystal planes from solutions in ethanol

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Abstract The adsorption of tetraethylammonium (TEA^+) ions on the (001) and $(01\bar{1})$ planes of the bismuth single crystal from solutions in ethanol has been investigated by impedance measurement method. The experimental data were obtained in 0.02 M mixed-electrolyte solutions and the calculations performed with electrode potential as the independent electrical variable. The Gibbs energy of adsorption of TEA^+ ions has been calculated using the simple virial adsorption isotherm, and it was found that the adsorption of TEA^+ cations is weaker than the adsorption of halide anions. The electroadsorption valency evaluated has a nearly constant value in the potential region studied. It was concluded that the formed effective surface dipole is significantly screened by the solvent molecules and the metal electron gas. The analysis of the impedance spectra was performed by fitting the experimental data to the various equivalent circuits. It was found that the behaviour of TEA^+ ions at $\text{Bi}(hkl)|\text{ethanol}$ interface can be described with the equivalent circuit, corresponding to the classical Frumkin–Melik-Gaikazyan model. The results obtained indicate that only weak interaction between TEA^+ ions and bismuth surface takes place, and there is no remarkable partial charge transfer from the adsorbed ions to the Bi surface atoms.

Keywords Adsorption · Tetraethylammonium ion · Bismuth · Ethanol · Impedance

Introduction

In our previous study [1], the adsorption of tetraethylammonium (TEA^+) cations on Bi(111) electrode from solutions in ethanol has been studied. It was found that in contrary to aqueous solutions, the adsorption of TEA^+ cations can be described using the traditional calculation methods for the adsorption of inorganic ions. This behaviour of the TEA^+ ions is apparently caused by the fact that the sizes of TEA^+ and solvated inorganic cations in ethanol are much closer than in the case of water. On the electrode surface, replacement of ethanol molecules with the TEA^+ ions should in turn accompany with much less change in dielectric properties of the electrical double layer than in aqueous solutions. The calculations, carried out for the TEA^+ cations [1] showed that the adsorption of these ions is generally weaker than adsorption of halide ions at the same interface. The obtained adsorption parameters allowed confirming that the specific interaction of TEA^+ ions with the electrode surface is weak, and the main reason of adsorption is the “squeezing out” effect of the large ions from the bulk of solution.

Although adsorption of tetraalkylammonium (TAA^+) cations has been of theoretical interest of electrochemists for a long time [2–8], it has been found in the latest years that the TAA salts can have important place also in applied electrochemistry because of their possible use in electrical non-aqueous double layer supercapacitors (EDLCs) [9–12]. Therefore, it is continuously of interest to establish the influence of the surface structure and composition of the TAA^+ ion to the adsorption behaviour of these ions from non-aqueous solutions. The main aim of the present study was to obtain the quantitative impedance data in the solutions of TEA salts in ethanol (i.e. in the system where

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the hydrocarbon chains in solvent molecules and adsorbing species are exactly the same) on the Bi(001) and Bi(01 $\bar{1}$) single crystal planes, i.e. on the surfaces that have different crystallographic structure from the Bi(111) plane and have higher adsorption activity. These data are very useful for the future understanding of adsorption processes occurring in non-aqueous EDLCs [10–12].

Experimental

The experimental procedure in the present work was exactly the same as in our previous study [1]. The Autolab PGSTAT 30 FRA 2 measuring system has been used for impedance measurements at the Bi(hkl)|ethanol interface. To obtain the data for calculating adsorption values and parameters, the series differential capacitance C of the electrode was measured at several ac frequencies f in the range from 0.5 to 300 Hz and in the potential region $-1.7 < E < -0.25$ V vs aqueous saturated calomel electrode (SCE), connected to the cell through a Luggin-like salt bridge. As was estimated in our earlier works [13–15], no irreversible changes occur on the electrode surface in the potential region $-1.7 < E < 0$ V (SCE) at all studied Bi single crystal planes in solutions of perchlorates in alcohols. To use the exactly applicable calculation methods, measurements were carried out in the mixed solutions $0.02x$ M TEAClO₄ + $0.02(1-x)$ M LiClO₄, i.e. at the constant ionic strength where LiClO₄ is the surface-inactive component and x denotes the mole fraction of TEAClO₄ in the mixture ($0.01 < x < 1$; ten solutions). In this region of potentials, no specific adsorption of Li⁺ ions occurs and the ClO₄⁻ ions undergo a very weak specific adsorption only at positively charged bismuth electrode surface from alcohols [14]. The low value of the electrolyte ionic strength used was caused by the limited solubility of TEAClO₄ in ethanol.

To obtain some information about mechanism and kinetics of the adsorption process of TEA⁺ ions, the impedance spectra for Bi(hkl) electrodes were measured at several potentials in the region $-1.7 < E < -0.25$ V vs SCE in pure 0.02 M LiClO₄ and TEAClO₄ solutions at 50 fixed different ac frequencies from 0.1 to 1×10^4 Hz. The results were used for fitting of the experimental data to the appropriate equivalent circuits.

The synthesis and subsequent treatment of TEAClO₄ was described in our previous work [1]. The high purity LiClO₄ (Aldrich, 99.99%) was used for the measurements without further purification. Commercial ethanol was treated with CaO and distilled. This procedure was repeated twice. According to the results of work [16], a very small amount of the residual water in ethanol does not influence the electrode capacitance and surface layer properties at the potential region where the impedance data were obtained

because the surface activity of C₂H₅OH at these potentials is noticeably higher than H₂O molecules.

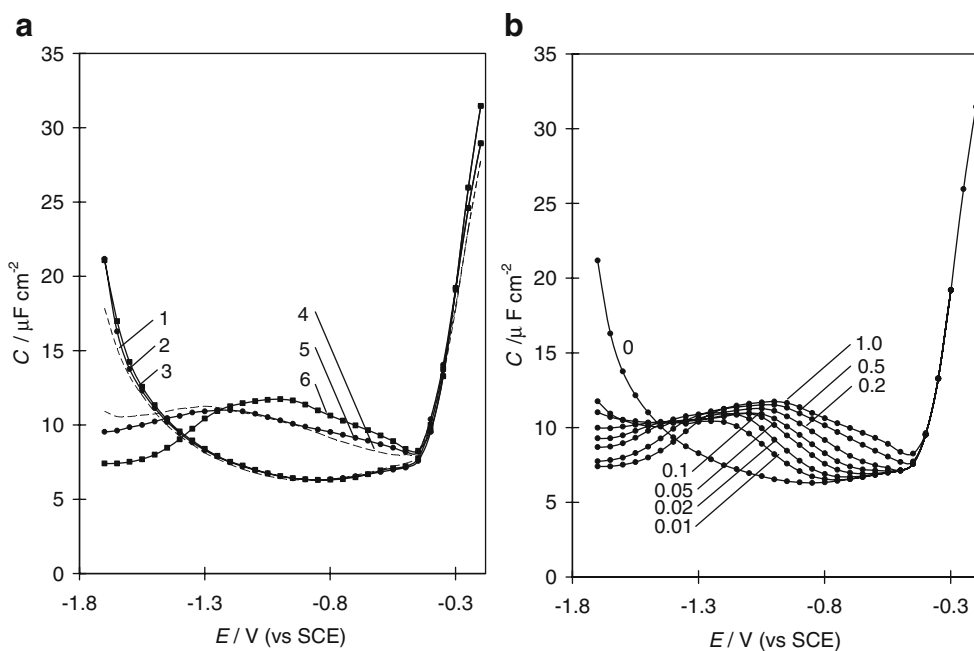
The preparation of single crystal Bi electrodes has been described elsewhere [17]. The final electrode surface preparation was obtained by the electrochemical polishing in the aqueous KI + HCl solution directly before measurements. Thereafter the electrode was carefully rinsed with ultra-purified (Millipore) water and ethanol and polarised at $E = -1.2$ V (against SCE) in the working solutions. All experimental details are more thoroughly described in our previous studies [13, 17–19].

Results

In Fig. 1a, C - E curves for 0.02 M LiClO₄ and TEAClO₄ measured at various Bi single crystal planes are presented. It can be seen from Fig. 1a that the shape of these curves for various planes is qualitatively similar. In TEAClO₄ solution, the differential capacitance rises then reaches maximum, and thereafter, at certain E , it begins to drop. The value of E , where the maximum occurs, and the values of C , however, depend on the single crystal plane studied. In Fig. 1b, C - E curves for the system Bi(01 $\bar{1}$)|0.02 x M TEAClO₄ + 0.02(1- x) M LiClO₄ in ethanol are shown. The quantity C in Fig. 1 is the low-frequency capacitance, obtained by extrapolating of the measured series capacitance C_s values to ac frequency $f=0$ using the $C_s - f^{1/2}$ plots. The $C_s - f^{1/2}$ function was selected for extrapolation because in the case of the adsorption of ions at Bi|ethanol interface, it has been found linear in the wide range of lower ac frequencies (0.5–200 Hz). In studies of the adsorption of halide ions on bismuth from alcohols, it was also found that the electrode charge values, calculated from extrapolated capacitances, were in very good agreement with the data obtained by chronocoulometry [15, 19]. As the dependence of C_s from f in the present case is much less expressed than in the case of adsorption of Cl⁻ or I⁻ ions, possible errors introduced by the extrapolation procedure should be minimal. According to the data in Fig. 1a at $E < -0.45$ V, there is a noticeable dependence of C on the Bi plane studied.

As was mentioned in [1], the C - E curves for TEA salts in ethanol are not only very different from C - E curves for TAA salts in aqueous solutions [5] but are also different from C - E curves for inorganic anions and cations in ethanol [13–16, 19]. It is necessary to continue with the studies of the reasons of the original shape of these C - E curves. In our previous study [1], it was proposed that it may be caused by the simultaneous changes of distances of inner and outer Helmholtz plane from the electrode surface. However, in the work [20], the analogous effect in the KNO₃+KF system was explained, relying on the

Fig. 1 Plot of differential capacitance C against electrode potential E for Bi(111) (1, 4), Bi(001) (2, 5) and Bi(011) (3, 6) electrodes in 0.02 M LiClO₄ (1–3) and 0.02 M TEAClO₄ (4–6) solutions in ethanol (a) and for Bi(011) electrode in solutions 0.02x M TEAClO₄+0.02(1-x) M LiClO₄ in ethanol with values of x given in the figure (b)



different dependence of the inner layer capacitance on the electrode potential. It can be seen from Fig. 1 that analogously to the case of Bi(111) plane, the C – E curves coincide at $E > -0.35$ V that makes it possible to obtain the electrode charge density values σ by means of the so-called back integration procedure. A comparatively simple method for calculation of the charge of specifically adsorbed cations σ_1 in these conditions (mixed electrolytes with the common counterion) was proposed independently by Hurwitz [21] and Dutkiewicz and Parsons [22] and is since known as the Hurwitz–Parsons–Dutkiewicz method.

It should be noted that it can be problematic to get quantitative results with the Hurwitz–Parsons–Dutkiewicz method for other (bigger or smaller) TAA cations because of different size problem of ions [23]. However, it is of interest to see qualitatively the difference in C – E curves for different TAA cations. For that reason, the C – E curves for 0.02 M tetrafluoroborates of tetraethylammonium (TEA), triethylmethylammonium (TEAM) and tetrabutylammonium (TBA) for Bi(001) plane in ethanol were measured. The results are presented in Fig. 2. Relying on data in Fig. 2, it is important to mention that the C – E curves for Bi(hkl)|non-aqueous electrolyte interface are more influenced by the size ratio effect than by the structure of TAA ions studied.

Discussion

Adsorption characteristics of TEA⁺ ions

It was shown in [1] that although possibility exists that systematic errors in the case of adsorption of TEA⁺ ions

may be larger than in the case of simple inorganic ions, the Hurwitz–Parsons–Dutkiewicz method [21, 22] is in principle applicable to the system Bi(111)|TEAClO₄+LiClO₄ in ethanol. The possible sources of errors [inequality of activity coefficients, inequality of the degrees of dissocia-

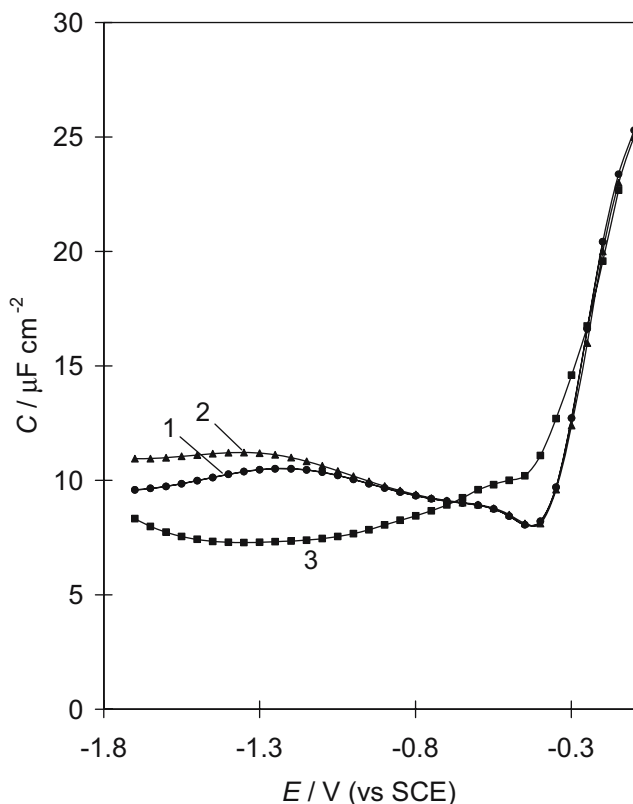


Fig. 2 Plot of differential capacitance C against electrode potential E for Bi(001) electrode in 0.02 M solutions of TEABF₄ (1), TEAMBF₄ (2) and TBABF₄ (3) in ethanol

tion (or ion pairing) and inequality of ionic radii for LiClO_4 and TEAClO_4 ions] were analysed, and it was found that the method [21, 22] is suitable for quantitative analysis. As the surface structure of the electrode does not have an effect on the possible errors of this method, the Hurwitz–Parsons–Dutkiewicz analysis can be also applied for the adsorption of TEA^+ ions on the $\text{Bi}(001)$ and $\text{Bi}(01\bar{1})$ single crystal planes from solutions $0.02x$ M $\text{TEAClO}_4 + 0.02(1-x)$ M LiClO_4 in ethanol.

The C – E curves for 0.02 M LiClO_4 solution were therefore integrated to establish the electrode charge σ using the potential of zero charge $E_{\sigma=0}$ as the starting point of the integration. The $E_{\sigma=0}$ values for $\text{Bi}(001)$ and $\text{Bi}(01\bar{1})$ single crystal planes in ethanol (–0.44 and –0.43 V against SCE, respectively) were estimated earlier [24] using the diffuse layer minimum potential in the C – E curves in diluted solutions of LiClO_4 in ethanol and confirmed lately by analogous measurements in solutions of LiBF_4 . For solutions containing TEA^+ ions, σ values were obtained by back integration started from $E = -0.25$ V, where the C – E curves coincide and the adsorption of TEA^+ ions is negligible.

The following calculations of adsorption characteristics were performed similarly to [1] and the other ionic systems [15, 18, 19, 25, 26]. In these studies it was found that although traditionally in the case of inorganic ions the electrode charge σ was used as the independent electrical variable, the electrode potential E could be equally well chosen for that variable. In the present study, like our previous work [1], we made calculations at $E = \text{const}$ because as a rule, E is used as independent variable in adsorption studies of organic compounds and analysis of data for non-aqueous EDLCs [9–12]. For the calculation of

charge of specific adsorption σ_1 , following the mixed electrolyte method [21, 22], the $\Delta\sigma = \sigma_o - \sigma$ values at constant E were calculated (σ_o is the charge density σ value in the LiClO_4 solution). Then by the integration of the $\Delta\sigma$ – E curves, the $\Delta\gamma$ – E curves were obtained, where $\Delta\gamma = \gamma_o - \gamma$, γ_o and γ are the specific surface work in the supporting electrolyte and in the solution containing TEA^+ ions, respectively. Next, the charge, due to specific adsorption of the TEA^+ ions, σ_1 was calculated according to the equation [22]

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

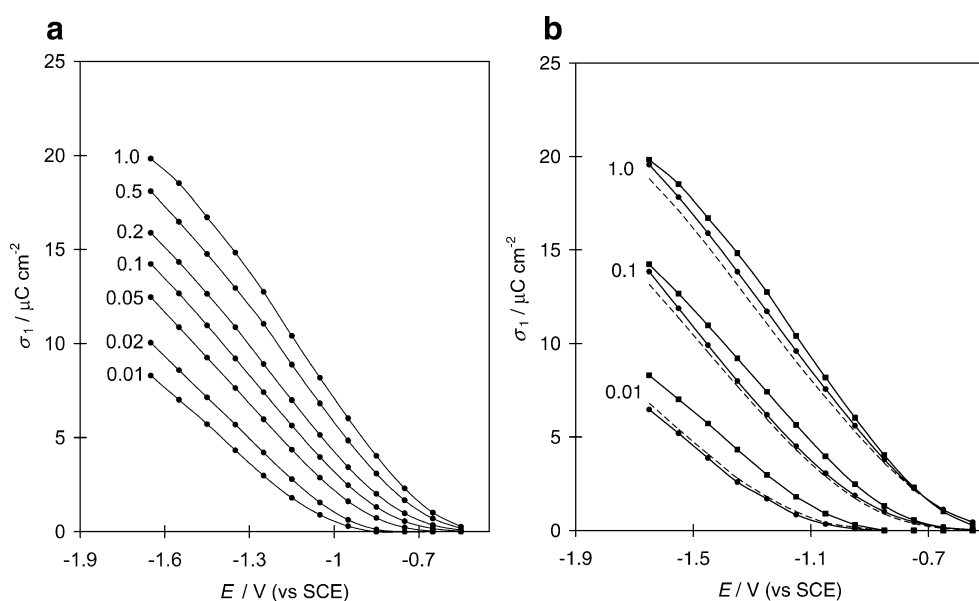
In Fig. 3a, the σ_1 – E curves at various x at the $\text{Bi}(01\bar{1})$ plane and in Fig. 3b, the σ_1 – E curves at some values of x at the different Bi planes in ethanol are shown. As can be seen from Fig. 3, the dependence of adsorption of TEA^+ from ethanol on the surface structure of the electrode is somewhat lower, and the adsorption is generally weaker than for inorganic anions adsorption at $\text{Bi}(hkl)$ planes [15, 25].

To calculate the Gibbs energy of adsorption $-\Delta G_A$, the σ_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 [27]

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

where z is the charge number of adsorbed anion ($z=+1$ in the present case), ϕ_2 is the potential drop in the diffuse layer, c is the total concentration of solution (0.02 M) and B is the second virial coefficient, characterising the mutual repulsion and size of the adsorbed ion. As follows from

Fig. 3 Plot of the charge σ_1 due to specifically adsorbed TEA^+ cations against electrode potential E for $\text{Bi}(01\bar{1})$ electrode in ethanol (**a**) and for $\text{Bi}(001)$ (filled circles), $\text{Bi}(01\bar{1})$ (filled squares) and $\text{Bi}(111)$ (dashed line; **b**) with values of x given in the figure



Eq. 2, if the isotherm adequately describes the adsorption process, the plots of $\ln(\sigma_1/zxc) + zF\phi_2/RT$ against σ_1 should be linear. However, as was found in our studies of adsorption of inorganic ions [13, 14, 26], in diluted nonaqueous solutions these plots are non-linear, and therefore, the isotherm parameters cannot be calculated. Instead, as it was found in many similar systems studied [1, 15, 19, 25], the formally good description of adsorption could be obtained using the semi-empirical simple virial isotherm

$$\ln(\sigma_1/zxc) = -\Delta G_A/RT - 2B_{\text{eff}}\sigma_1/z, \tag{3}$$

and the plots of $\ln(\sigma_1/zxc)$ against σ_1 for Bi(hkl) | nonaqueous ionic system were linear. The contradictions in the use of virial isotherm is comprehensively analysed in our previous study [26]. It was shown that the traditional method of calculation of ϕ_2 potential in the presence of adsorbed ions is not justified and as a possible reason for that the concept of ion-pairing in the inner part of double layer was proposed. The second virial coefficient in Eq. 3 is named B_{eff} to emphasize that its values have not explicit physical meaning and can only be used for qualitative comparison of mutual interaction of adsorbed ions in different systems. However, as was shown in [18, 26], at $\sigma=0$ and $\sigma_1 \rightarrow 0$ isotherm (2) takes the form of isotherm (3), and therefore, the parameter $-\Delta G_A$, obtained from isotherm (3) for uncharged surface, can be used for further quantitative treatment.

In Fig. 4, the plots corresponding to Eq. 3 for Bi(001) and Bi(01 $\bar{1}$) plane are presented. As can be seen from Fig. 4, similarly to Bi(111) plane [1] the linear and almost parallel plots are obtained. This permits to calculate the

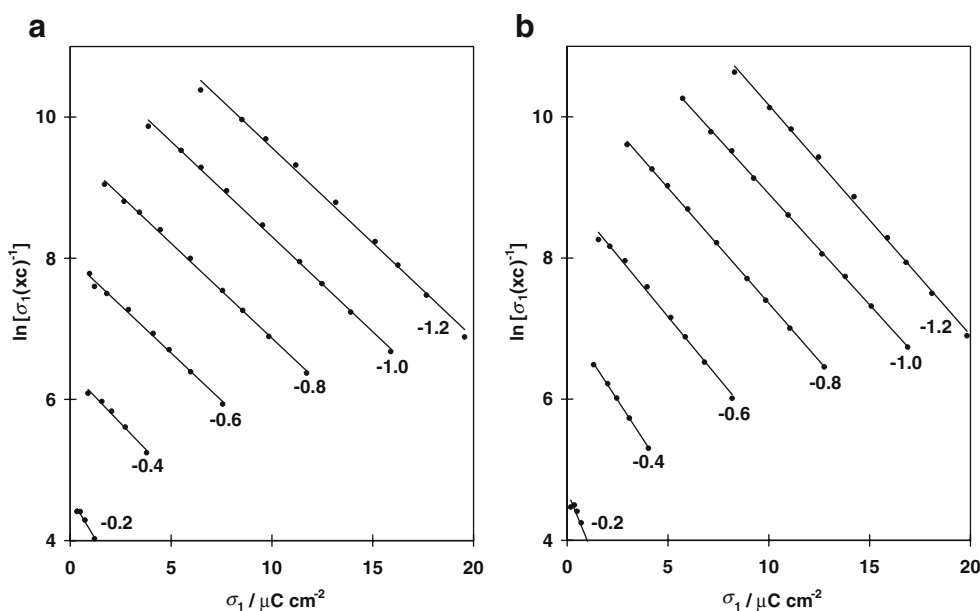
adsorption parameters of TEA⁺ cations at Bi(hkl) | nonaqueous electrolyte interface. Nevertheless, it must be mentioned, that the virial isotherm was chosen to maintain the similarity of the description of the adsorption of TEA⁺ cations and inorganic anions in ethanol. However, in the present case, because of the large size of TEA⁺ cations, it can be more correct to use the Frumkin isotherm

$$\ln\{\theta/(1-\theta)/xc\} = -\Delta G_A/RT + 2a\theta, \tag{4}$$

where $\theta = \Gamma/\Gamma_{\text{max}}$, Γ being the surface excess of adsorbed ions ($\Gamma = \sigma_1/zF$, Γ_{max} is the Γ value when the surface is fully covered with adsorbed particles) and a is the equivalent of B in virial isotherm, i.e. the parameter characterising the mutual interaction of adsorbed particles. The corresponding plots for Bi(01 $\bar{1}$) plane are presented in Fig. 5. It can be seen from Figs. 4 and 5 that although the θ values are more than 0.5 (assuming the hexagonal package with $r_{\text{TEA}} = 0.40$ nm [28]), the virial and Frumkin isotherms lead to very similar plots. It means that taking into account the saturation value of σ_1 becomes important at higher values of θ than surface coverages used in the present work. Therefore, the use of virial isotherm, common for the description of ionic systems, seems to be justified in the present case at least as the first approximation.

According to Eq. 3, the extrapolation of the straight lines in Fig. 3 to the condition $\sigma_1=0$ yields to $-\Delta G_A$ for given electrode potential. The $-\Delta G_A$ values were calculated using the common standard conditions for the virial isotherm (1 ion cm⁻² on the electrode surface and 1 mol 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. The $-\Delta G_A^0$ values ($-\Delta G_A$ at $E = E_{\sigma=0}$) for the adsorption of TEA⁺ ions for

Fig. 4 Plot of the function $\ln(\sigma_1/zxc)$ against the charge σ_1 of specifically adsorbed TEA⁺ cations at the Bi(001) | ethanol interface (a) and at the Bi(01 $\bar{1}$) | ethanol interface (b) at constant electrode potential. The electrode potential E/V (vs $E_{\sigma=0}$) is given in the figure



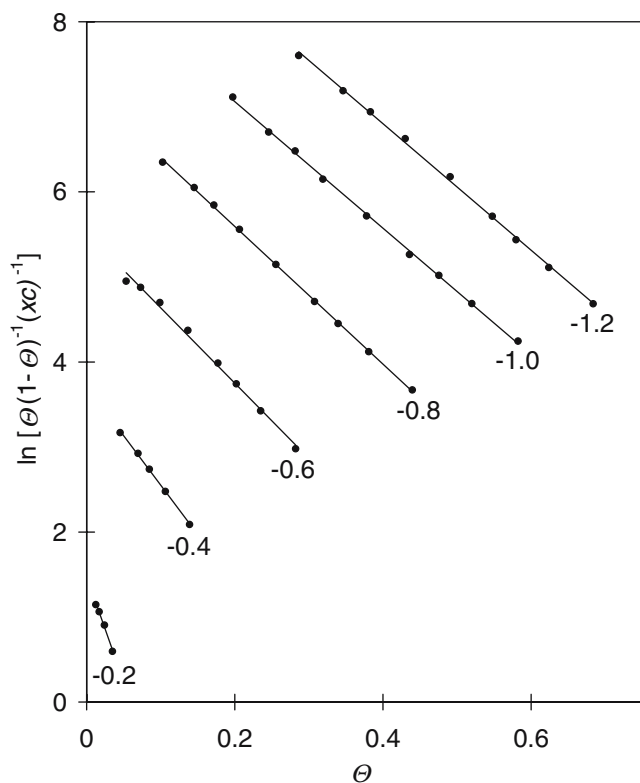


Fig. 5 Plot of the function $\ln[\theta/(1-\theta)xc]$ against the surface coverage θ of specifically adsorbed TEA^+ cations at the $\text{Bi}(01\bar{1})|\text{ethanol}$ interface at constant electrode potential. The electrode potential E/V (vs $E_{\sigma=0}$) is given in the figure

various Bi single crystal planes are presented in Table 1. As it was shown in [26] 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, as this value at $E = E_{\sigma=0}$ is independent on c and the $-\Delta G_A^0$ values are the same for different modifications of virial isotherm. For the sake of comparison, in Table 1, alongside with the adsorption and inner layer parameters for TEA^+ cations at the $\text{Bi}(001)$ and $\text{Bi}(01\bar{1})$ planes, the same parameters for TEA^+ cations at the $\text{Bi}(111)$ plane [1] and also for Cl^- anions [25] are presented. It is seen from Table 1 that the $-\Delta G_A^0$ values for TEA^+ cation are close to this value for Cl^- anion. As is typical for ions with comparatively weak adsorption at $\text{Bi}|\text{ethanol}$ interface [25], the differences in $-\Delta G_A^0$ values at various planes are very small. As was expected, the second virial coefficient B_{eff} values for TEA^+ ions is significantly higher than that of Cl^- because of large dimensions of the TEA^+ ions.

The obtained adsorption data were used for the calculation of the electrosorption valency (formal charge transfer coefficient) values γ' [29] according to the formula [30]

$$\gamma' = (1/F)(\partial\Delta G_A/\partial E)_\Gamma = -(1/F)(\partial\sigma/\partial\Gamma)_E. \quad (5)$$

For the calculation of γ' by the second part of Eq. 5, the σ - σ_1 plots at constant E were constructed as shown in

Fig. 6. As can be seen in Fig. 6, the σ - σ_1 plots for the adsorption of TEA^+ ions on $\text{Bi}(001)$ plane represent straight lines that are nearly but not exactly parallel as in the case of $\text{Bi}(111)$ plane. The tendency of a decrease in the slope of the plots with the rise of E can be mentioned. According to the second part of Eq. 4, the slope values of these plots yield $\gamma' = 0.20$ – 0.23 . Therefore, γ' for the present systems depends very slightly on E in the range of potentials studied and has approximately the same value as in the case of $\text{Bi}(111)$ plane. The γ' values can also be obtained by first part of Eq. 4. Thus, if we consider the ΔG_A - E dependence as linear, we get the constant γ' values which can be taken as mean values of this parameter. As follows from Table 1, the γ' values for TEA^+ cations are more than twice lower than for Cl^- anions. The small γ' values are in accordance with a small geometric factor in the case of large ions. The low value of γ' and only slight dependence of γ' from E means that the specific interaction of TEA^+ cations with the Bi surface is weak, and the adsorption is mainly caused by the “squeezing out” effect of large TEA^+ cations from the bulk of solution, similarly to the $\text{Bi}(111)$ plane [1].

To characterise the inner layer properties in the case of TEA^+ ions adsorption on the $\text{Bi}(001)$ and $\text{Bi}(01\bar{1})$ planes, the values of the surface dipole μ_s , created by an adsorbed

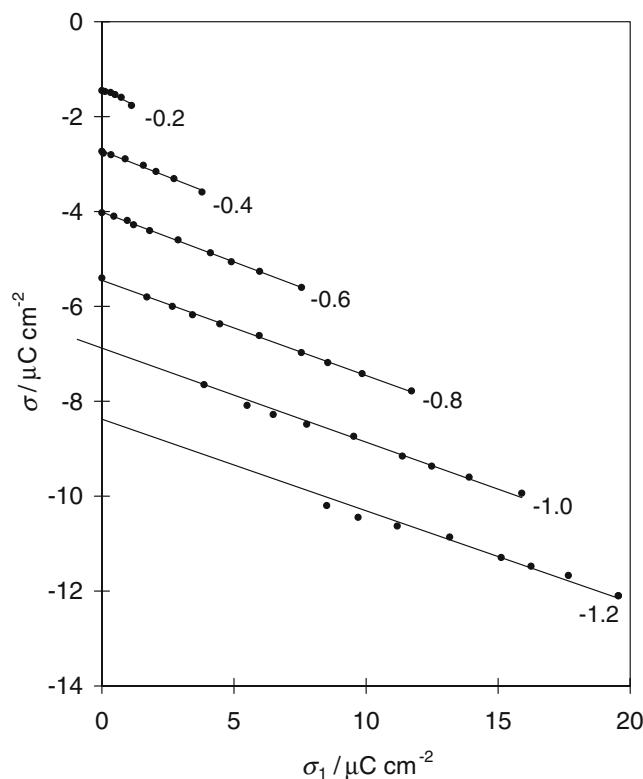


Fig. 6 Plot of the electrode charge σ against the charge σ_1 of specifically adsorbed TEA^+ cations at the $\text{Bi}(01\bar{1})|\text{ethanol}$ interface. The electrode potential E/V (vs $E_{\sigma=0}$) is given in the figure

Table 1 The adsorption and inner layer characteristics for the TEA⁺ and Cl⁻ ions adsorbed on the Bi single crystal planes in ethanol

Electrode	Parameter	Condition	TEA ⁺	Cl ⁻ [24]
Bi(111), [1]	$-\Delta G_A^0$ (kJ mol ⁻¹)	$E = E_{\sigma=0}$	81.0	81.7
	B_{eff} (nm ² ion ⁻¹)		2.7	0.9
	γ'		0.225	0.51
	$10^{30}\mu_s$ (C m ion ⁻¹)	$E = E_{\sigma=0}$	5.8	4.1
Bi(001)	$-\Delta G_A^0$ (kJ mol ⁻¹)	$ E \gg E_{\sigma=0} $	13.7	3.6
	B_{eff} (nm ² ion ⁻¹)	$E = E_{\sigma=0}$	81.5	82.2
	γ'		2.2	0.7
	$10^{30}\mu_s$ (C m ion ⁻¹)	$E = E_{\sigma=0}$	0.21	0.52
Bi(011)	$-\Delta G_A^0$ (kJ mol ⁻¹)	$ E \gg E_{\sigma=0} $	8.2	3.5
	B_{eff} (nm ² ion ⁻¹)	$E = E_{\sigma=0}$	13.9	2.9
	γ'		81.9	82.3
	$10^{30}\mu_s$ (C m ion ⁻¹)	$E = E_{\sigma=0}$	2.4	0.8
	$-\Delta G_A^0$ (kJ mol ⁻¹)	$ E \gg E_{\sigma=0} $	0.22	0.49
	B_{eff} (nm ² ion ⁻¹)		8.7	3.8
	γ'		13.6	2.8
	$10^{30}\mu_s$ (C m ion ⁻¹)			

anion and its image charge in the metal [31, 32], were calculated according to Eq. 6

$$\mu_s = ze_0\varepsilon(1 - \gamma'/z)/K_{02}, \tag{6}$$

where e_0 is the elementary charge, ε is the dielectric permittivity and K_{02} is the inner layer integral capacitance. To obtain K_{02} values, the measured potential values $E - E_{\sigma=0}$ were plotted vs σ_1 , extrapolated to $\sigma_1=0$ at constant σ (these values are practically equal to $E - E_{\sigma=0}$ in LiClO₄ solutions except at the highest negative potentials where the slow hydrogen evolution reaction causes pseudo-capacitance to appear) [1]. The potential drop in the diffuse layer ϕ_2 was then subtracted from $E - E_{\sigma=0}$ at $\sigma_1=0$ to get the potential drop in the inner layer $\Delta\phi^{M-2}$. K_{02} values were calculated according to the equation

$$K_{02} = \sigma/\Delta\phi^{M-2}. \tag{7}$$

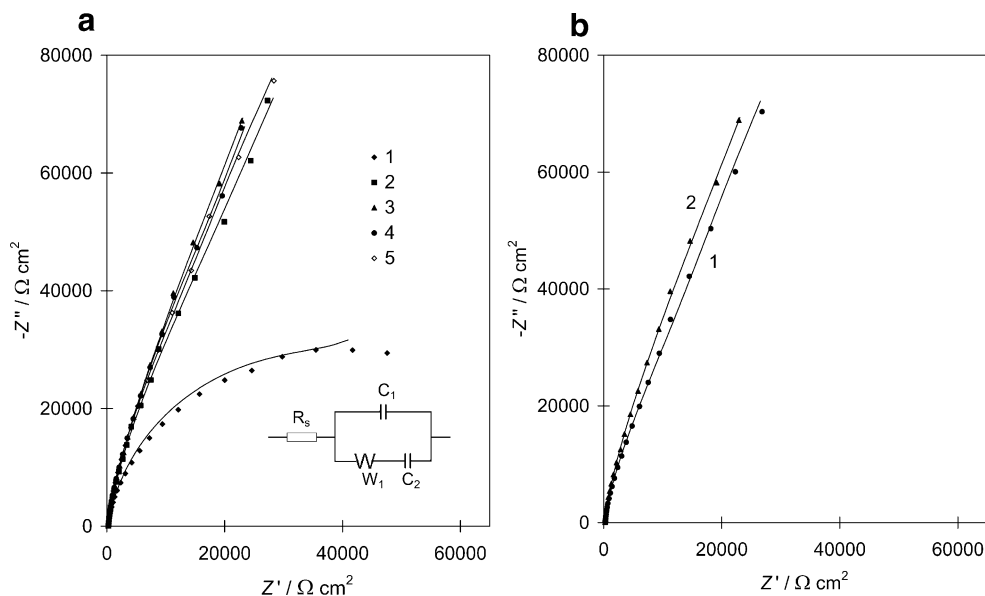
As the γ' value in the present case depends very little on E , the mean value of γ' was used in Eq. 6. The effective dipole moment values of adsorbing species μ_s , calculated at $\sigma=0$ and at $\sigma \ll 0$ for TEA⁺ ions adsorption from ethanol on Bi planes by Eq. 6 are presented in Table 1. The corresponding data for the Bi(hkl)|ethanol/Cl⁻ system are included for comparison. The permittivity of the inner layer ε was taken equal to that of a vacuum ($8.85 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$) [32]. In general, the values of μ_s , obtained for TEA⁺ as well as for halides adsorbed at Bi planes from all solvents studied, are smaller than the values calculated for a dipole formed by a charged ideal sphere of an ionic radius r_i ($r_{\text{TEA}^+} = 0.40 \text{ nm}$ [28]) adsorbed at the perfect conductor (for $\text{TEA}^+ \mu_s = 64 \times 10^{-30} \text{ C m}$). The low values of μ_s are usually explained with the screening of dipole created by an adsorbed ion and its image charge in the metal by the

solvent molecules and ions in the diffuse layer as well as by the metal electrons [15, 18, 25, 29–32]. This effect may be caused also by the transfer of electronic charge from the ion to the metal [31] but it is less probable for the present systems because there is no noticeable partial charge transfer. If there is a strong specific interaction of ions with the electrode surface, then the significant shift of the charge centre of TEA⁺ ions at the negative surface charge and the decrease in μ_s should be observed. In fact, in the present case, μ_s rises somewhat at $E \ll E_{\sigma=0}$, indicating the absence of significant specific interaction of TEA⁺ ions with the bismuth electrode surface. The rise of μ_s can be associated with the decrease in screening of the dipole with the solvated ions and solvent molecules in the diffuse layer because of the increasing distance of outer Helmholtz plane from electrode surface x_2 at $E \ll E_{\sigma=0}$, where x_2 is determined mainly by the dimensions of solvated Li⁺ ions that are larger than the radius of ClO₄⁻ ions. In addition, the adsorption of large TEA⁺ cations at $E < E_{\sigma=0}$ in turn increases x_2 .

Analysis of impedance spectra

The impedance spectra for 0.02 M TEAClO₄ solutions in ethanol at some selected potentials for Bi(011) plane are presented in Figs. 7a and 8a. In Figs. 7b and 8b, the impedance spectra in 0.02 M TEAClO₄ and 0.02 M LiClO₄ solutions for the same electrode at $E = -1.2 \text{ V}$ are shown. The points represent experimental data; the lines describe the results, obtained by fitting of the experimental data to a certain equivalent circuit. The fitting procedure and the selection of the circuit will be described below. In Fig. 7 the complex impedance plane (Z'' vs Z') plots (so-called Nyquist plots) are shown, where Z' is the real part and Z'' is the imaginary component of the impedance

Fig. 7 Complex plane plots in ethanol (*points*, experimental data; *solid lines*, fitting results) for the interface Bi(011) | 0.2 M TEAClO₄ at E/V (vs $E_{\sigma=0}$): 1, -1.6; 2, -1.4; 3, -1.2; 4, -1.0; 5, -0.8 (a) and for the interfaces Bi(011) | 0.2 M LiClO₄ (1) and Bi(011) | 0.2 M TEAClO₄ (2) at $E=-1.2$ V (b). *Inset*: the equivalent circuit used for fitting the experimental data (R_s , solution resistance; C_1 , “true” double layer capacitance; C_2 , adsorption capacitance; W_1 , Warburg-like diffusion impedance)



($Z'' = 1/jC_s\omega$; $j = \sqrt{-1}$, C_s is the series capacitance of the system and $\omega = 2\pi f$ is the angular frequency). In Fig. 8 the phase angle vs logarithm of applied ac frequency is plotted. It is seen from Figs. 7 and 8 that for the given plane, only a slight dependence of these curves on E exists in the potential region where the adsorption of TEA⁺ ions takes place. At potentials $E < -1.5$ V, an additional faradaic process—probably the hydrogen evolution—begins, and by that reason, the spectra at $E = -1.6$ V are somewhat different. This behaviour of impedance spectra is similar for all Bi single crystal planes studied.

To obtain some quantitative kinetic characteristics of the adsorption of TEA⁺ ions at the interface Bi(hkl) | ethanol,

the experimental results were fitted to various equivalent circuits (EC) using a non-linear least squares fitting minimisation method [33, 34]. A computer programme named ‘Zview2’ was used for that purpose [35]. For the EC, given in Fig. 7a, this programme permits to get the values for the following parameters: the electrolyte resistance R_s , the high-frequency or “true” capacitance C_1 , the adsorption capacitance, caused by the dependence of Gibbs adsorption Γ on E , C_2 and the generalised Warburg element characteristics—the limiting diffusion resistance W_1-R , the parameter W_1-T equal to L^2/D , where L is the effective diffusion layer thickness and D is the effective diffusion coefficient of the particles, and the fractional exponent

Fig. 8 Dependence of phase angle δ on ac frequency in ethanol (*points*, experimental data; *solid lines*, fitting results) for the interface Bi(011) | 0.2 M TEAClO₄ at E/V (vs $E_{\sigma=0}$): 1, -1.6; 2, -1.4; 3, -1.2; 4, -1.0; 5, -0.8 (a) and for the interfaces Bi(011) | 0.2 M LiClO₄ (1) and Bi(011) | 0.2 M TEAClO₄ (2) at $E=-1.2$ V (b)

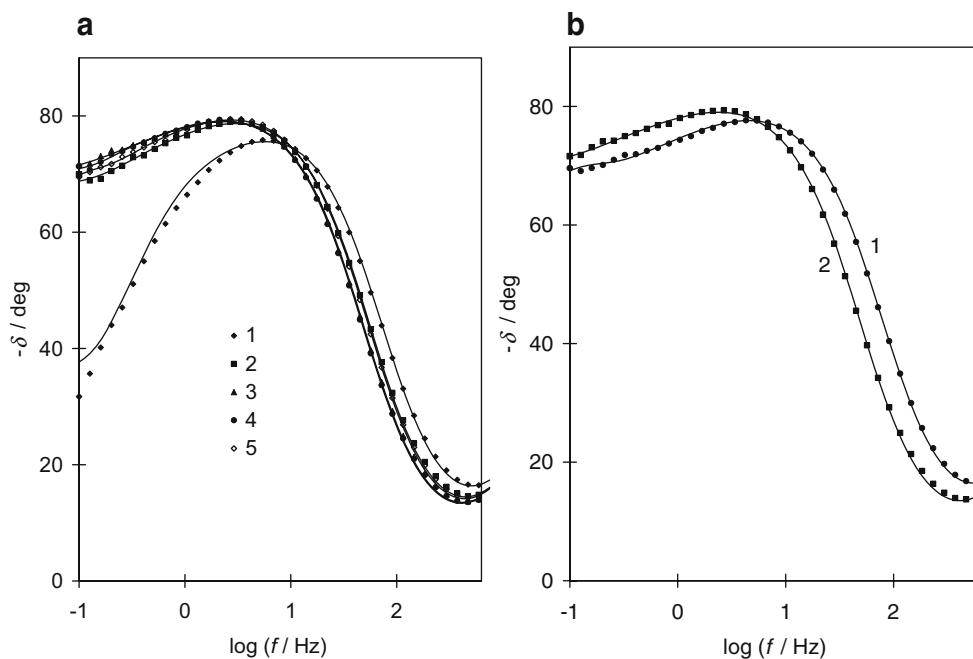


Table 2 Values of fitting parameters for the systems $\text{Bi}(01\bar{1})|0.02\text{ M TEAClO}_4$ and $\text{Bi}(01\bar{1})|0.02\text{ M LiClO}_4$ in ethanol at $E=-1.2\text{ V}$ for the Frumkin–Melik-Gaikazyan model (EC in Fig. 7a)

Element	TEAClO ₄		LiClO ₄	
	Value	Error%	Value	Error%
$10^4\chi^2$	1.75		1.48	
R_s ($\Omega\text{ cm}^2$)	286	6.5	263	8.5
C_1 ($\mu\text{F cm}^{-2}$)	11.5	0.6	7.4	0.5
C_2 ($\mu\text{F cm}^{-2}$)	70.4	18	39.2	10.1
W_1-R ($\Omega\text{ cm}^2$)	3.1×10^5	9.2	2.5×10^5	5.9
W_1-P (fixed)	0.5		0.5	

W_1-P varying between 0 and 1. In the case of present system, the last parameter is suitable to fix to 0.5 [25, 36, 37]. The goodness of the fit was estimated by the value of chi-square (χ^2) function, weighted sum of squares (Δ^2) and by relative errors of each parameter of elements in EC.

Previously it was found that in the bismuth|ethanol systems where no adsorption occurs or adsorption is weak (the LiClO_4 |ethanol [36] and LiCl |ethanol systems [25] as well as for the LiI |ethanol system [37] in the region of potentials where the adsorption of Γ^- was relatively weak and could be described with traditional adsorption models), the simplest EC giving the satisfactory fitting results was EC, shown in Fig. 7a, i.e. the EC analogous to the classical Frumkin–Melik-Gaikazyan (FMG) model [38, 39]. The original FMG model [39] was worked out for the description of the kinetics of the adsorption of the organic compounds on the electrodes. As can be seen from Figs. 7 and 8, the coincidence of experimental and calculated curves is very good (except at $E=-1.6\text{ V}$, where an additional process takes place). The applicability of the FMG model in the case of the adsorption of halide ions [25, 36, 37] is interesting because the physical conditions of original FMG theory [39] were much different from those of simple ionic system. Nevertheless, the FMG model and the modifications of that were found to describe the behaviour of ionic systems also on other metals [38, 40]. In the present case, the classical FMG model gave the best description of the system. No one of the attempts to use the more complex ECs led to significant improvement of the fit. The frequently used [38, 40] Ershler model [41] (traditionally called as combined FMG and Randles model), where into the so-called adsorption branch the adsorption resistance R_{ad} has been added, did not lead neither to the diminishing of χ^2 function nor to the decrease in errors in individual parameters. As in the case of Cl^- ions [25], the results of fitting of our results to EC, corresponding to the Ershler model, yield the very low R_{ad} values ($R_{\text{ad}} < 1\ \Omega\text{ cm}^2$, indicating to the physically reversible adsorption) and the error values for that are extremely high. Therefore, the parameter R_{ad} is negligible and the Ershler model has no

advantage ahead of the classical FMG model. This result indicates that in ethanol the TEA^+ ions behave similarly to simple inorganic ions. The theory of Grafov, Damaskin and Baturina model [42], worked out for mixed electrolyte solutions, seems also a bit too complicated for the present system because we performed the impedance analysis in pure TEAClO_4 solution only (the mixed solutions were used for calculations of adsorption only). Therefore, it should be concluded that the classical FMG circuit is most preferable EC for the description of the investigated systems in ethanol, and the adsorption of TEA^+ ions is reversible on $\text{Bi}(\text{hkl})$ from ethanol.

As the Nyquist plots and the phase angle-log f plots at various potentials between $-1.4 < E < -0.8\text{ V}$ almost coincide, the parameters, obtained by fitting, are also almost independent of electrode potential. In Table 2, some of the fitting parameters for 0.02 M TEAClO_4 solution on $\text{Bi}(01\bar{1})$ plane at $E=-1.2\text{ V}$ are presented together with the same parameters for LiClO_4 solutions. The data in Table 2 confirm the conclusion made from Figs. 7 and 8 that the FMG model describes the system very well (with χ^2 function less than 2×10^{-4} and the errors of individual parameters are mainly less than 10%). Therefore, as in the case of Cl^- ions adsorption [25], it can be assumed that in the whole region of potentials studied, the TEA^+ ions retain their charge, and as a first approximation, adsorption can be regarded as a physical adsorption. The most interesting result in Table 2 is the rise of the high-frequency capacitance C_1 compared with LiClO_4 solution, the fact that together with the absence of R_{ad} indicates that the adsorption of TEA^+ ions in ethanol is fast and reversible and therefore can be regarded to be similar to the adsorption of simple ions [25]. Unlikely of anions, the fitting parameters were found to be only comparatively weakly dependent on the single crystal plane studied.

Conclusions

It was found that the adsorption activity and adsorption parameters of tetraethylammonium cations on $\text{Bi}(001)$ and $\text{Bi}(01\bar{1})$ single crystal planes are similar to those for $\text{Bi}(111)$ plane. The standard Gibbs energy values of adsorption on the uncharged Bi single crystal planes for tetraethylammonium cations are close to those for Cl^- anions but significantly lower than in the case of adsorption of Br^- and Γ^- anions. The electrosorption valency calculated for the present systems was found to be almost independent of the electrode potential. The low values of the effective dipole moment formed by an adsorbed tetraethylammonium ion and its image charge show that the dipole is significantly screened by the “free” electrons in the metal and by the ions and solvent molecules in the diffuse layer.

The increase in the effective surface dipole values at higher negative potentials was explained by the lower screening in the conditions where the distance of outer Helmholtz plane from electrode surface increases as a result of adsorption of large cations.

The analysis of the impedance spectra was performed by fitting the experimental data to the various equivalent circuits. It was found that almost in the whole potential region where the adsorption of tetraethylammonium ions occurs, the interface characteristics, obtained by fitting, depend only slightly on electrode potential. It was found that the behaviour of tetraethylammonium ions at Bi (hkl)|ethanol interface can be well described with the equivalent circuit, corresponding to the classical FMG model.

The results obtained confirm that the specific interaction of tetraethylammonium ions with the electrode surface is weak, and the main reason of adsorption is the “squeezing out” effect of the large ions from the bulk of solution. There seems to be no strong interaction between tetraethylammonium ions and bismuth surface, and the partial charge transfer from the ions to the Bi surface atoms can be neglected in the systems studied.

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