

IMPEDANCE STUDY OF ADSORPTION OF CHLORIDE IONS IN ETHANOL ON Bi(001) SINGLE CRYSTAL PLANE

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Dedicated to Professor Sergio Roffia on the occasion of his retirement.

The impedance spectra for Bi(001) single crystal plane in 0.1, 0.02 and 0.003 M LiCl solutions in ethanol have been measured. It was found that reproducible experimental data for Bi electrode in ethanol solutions could be obtained at ac frequencies between 0.1 and 10 000 Hz and electrode potentials from -1.6 to -0.2 V (*vs* saturated calomel electrode). Outside this potential region, faradaic processes were detected. By fitting the experimental data to various equivalent circuits it was found that the Frumkin-Melik-Gaikazyan model yields good fit in almost the whole potential range studied. Using this model the dependences of "true" and adsorption capacitance as well as diffusion resistance on electrode potential have been obtained. 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 electric variables. The Gibbs energy of adsorption of Cl⁻ ions has been calculated using a simple virial adsorption isotherm. It was found that the adsorption of Cl⁻ anion increases in the order methanol < ethanol < propan-2-ol. It was found that on the Bi(001) plane the electroadsorption valency has a constant value in the potential range studied. It was concluded that the formed effective surface dipole is significantly screened by the solvent molecules and the metal electron gas.

Keywords: Electrochemistry; Ethanol; Impedance spectroscopy; Ionic change; Adsorption capacitance; Bismuth; Thermodynamics.

In recent years, in addition to using electrochemical impedance data for obtaining thermodynamic adsorption characteristics of various compounds on electrodes, the method has become popular because it permits to study the mechanism and kinetics of adsorption of ions. So far, these investigations have been restricted mainly to aqueous solutions. Taking into account that we have studied the adsorption of inorganic ions from non-aqueous solvents for a long time¹⁻⁵, it is of interest to analyse the impedance data for non-aqueous systems in more detail. The aim of the present work is to

obtain the impedance and adsorption characteristics of Cl^- ions on the Bi(001) single crystal plane in LiCl solutions in ethanol. In contrast to I^- ions, showing strong adsorption on Bi electrodes with different surface characteristics⁶⁻⁹ in various alcohols, adsorption of Cl^- ions is relatively weak in these solvents^{3,10}. For I^- ions it was found, that for all Bi single crystal planes studied at electrode potentials where the surface charge exceeds $15\text{--}20 \mu\text{C cm}^{-2}$, partial charge transfer from I^- ions to Bi surface atoms takes place and the formation of a surface compound is probable. It is therefore interesting to investigate the possibility of existence of this phenomenon also in the case of weaker adsorption of Cl^- ions.

EXPERIMENTAL

The impedance spectra for Bi(001) electrode in 0.1, 0.02 and 0.003 M LiCl solutions in ethanol were measured mainly at ac frequencies $0.1 < f < 1 \times 10^4$ Hz (in some experiments $0.05 < f < 1 \times 10^5$ Hz) at 50–70 different frequencies using the Autolab PGSTAT 30 FRA 2 measuring system in the potential region $-1.4 < E < -0.2$ V vs aqueous saturated calomel electrode (SCE), connected to the cell through a salt bridge. As it was found previously, no irreversible changes occur on the electrode surface in this potential region. For calculation of the charge of specifically adsorbed Cl^- anions, the differential capacitance of electrode was measured at several frequencies in the range of $20 < f < 300$ Hz in the solutions containing 0.1x M LiCl and 0.1(1 - x) M LiClO_4 , i.e. at the constant ionic strength where x denotes the mole fraction of LiCl in the mixture. The mole fraction of LiCl was varied from 0.001 to 0.1 and LiClO_4 was regarded as a surface-inactive component. As it was found¹¹, the ClO_4^- ion undergoes a very weak specific adsorption at positively charged planes of bismuth single crystal from alcohols, but its surface activity is much lower than for halide anions. LiClO_4 was purified by double recrystallisation from ethanol and dried by heating in vacuum. The high-purity LiCl was used for the measurements without further purification. Commercial ethanol was treated with CaO and distilled. This procedure was repeated twice. According to our previous work¹, a very small amount of the residual water in ethanol does not influence the electrode capacitance in the potential region where the impedance data were obtained.

The preparation of single crystal Bi electrodes has been described elsewhere^{3,12}. The final electrode surface preparation was obtained by electrochemical polishing in aqueous KI-HCl solutions before measurements. Thereafter the electrode was carefully rinsed with ultra-purified (Millipore) water and ethanol and polarised at $E = -1.2$ V (vs SCE) in the working solutions.

All experimental details are more thoroughly described in our previous studies^{2-4,12}.

RESULTS

In Fig. 1, C - E curves for the system Bi(001)|0.1x M LiCl and 0.1(1 - x) M LiClO_4 are shown. The values of C in Fig. 1 are obtained by extrapolating the measured serial capacitance, C_s , to $f = 0$ using the C_s - $f^{1/2}$ plots that are linear in the range of frequencies 20–300 Hz. It can be seen from Fig. 1 that

the adsorption of Cl^- ions begins at potentials about 0.4 V more positive than the adsorption of I^- ions⁹. While there were characteristic maxima on the C - E curves for solutions containing I^- ions, in the case of Cl^- ions maxima occur only at the two highest concentrations of LiCl.

The impedance spectra for LiCl solutions at some selected potentials are presented in Figs 2–4. The points represent experimental data; the lines describe the results, obtained by fitting the experimental data to a certain equivalent circuit. The fitting procedure and the selection of the circuit will be described in the following section. The plots correspond mainly to the system $\text{Bi}(001)|0.1 \text{ M LiCl}$ in ethanol, but some curves for concentrations 0.02 mol l^{-1} are also presented. In Fig. 2 the complex plane (Z' vs Z'') plots (Nyquist plots) for different electrode potentials are shown, where Z' is the real part and Z'' is the imaginary component of the 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. 3 the same data are presented in the Cole–Cole representation, $1/(\omega R_p)$ vs C_p , where R_p and C_p are the parallel resistance and capacitance of the interface, respectively. In Fig. 4 the phase angle δ vs ac frequency plots for the same system are given. These curves are similar when the adsorption is absent, but depend significantly on electrode potential in the region where the adsorption of Cl^- ions occurs. Changing the

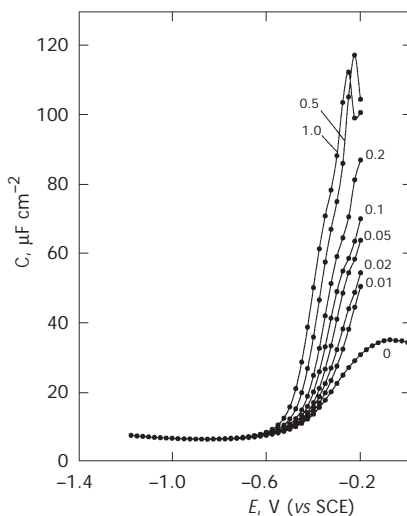


FIG. 1

Differential capacitance curves for $\text{Bi}(001)$ electrode in solutions $0.1x \text{ M LiCl}$ and $0.1(1 - x) \text{ M LiClO}_4$ in ethanol. The values of x are given

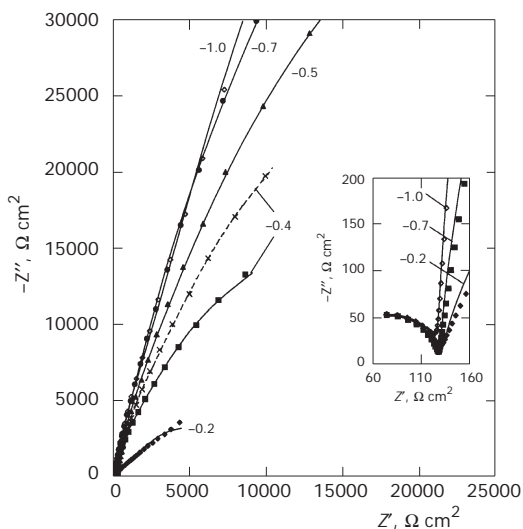


FIG. 2

Complex plane plots for the interface Bi(001)|LiCl (concentration c) in ethanol (points, experimental data; solid lines, fitting results for $c = 0.1 \text{ mol l}^{-1}$; dashed line, fitting result for $c = 0.02 \text{ mol l}^{-1}$). The electrode potential E , V (vs SCE) is given. The inset shows the high-frequency part of the same plots

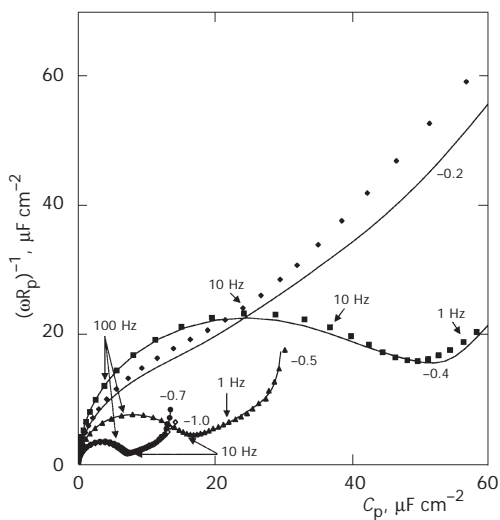


FIG. 3

Dependence of function $(\omega R_p)^{-1}$ on parallel capacitance C_p (Cole-Cole plots) for the interface Bi(001)|LiCl ($c = 0.1 \text{ mol l}^{-1}$) in ethanol (points, experimental data; solid lines, fitting results). The electrode potential E , V (vs SCE) is given

concentration of the solution shifts curves in the frequency scale but does not change their shape.

DISCUSSION

Analysis of Impedance Spectra

To analyse quantitatively the behaviour of LiCl at the interface Bi(001)|ethanol, the results were fitted to various equivalent circuits (EC) using a non-linear least-squares fitting minimisation method^{13,14}. A computer program Zview2 was used for that purpose¹⁵. The goodness of the fit was estimated by the value of χ^2 function and by relative errors of each parameter of elements in EC.

It was found that in the LiClO₄|ethanol system¹⁶ the simplest EC giving the satisfactory fitting results was EC in Fig. 5a, based on the classic Frumkin–Melik-Gaikazyan model^{17–20}. In the case of the Frumkin–Melik-Gaikazyan model, the impedance and capacitance functions have the following forms

$$Z(\omega) = R_s + \{j\omega C_1 + 1/[(\sigma_{ad}/\sqrt{j\omega}) + (1/j\omega C_2)]\}^{-1} \quad (1)$$

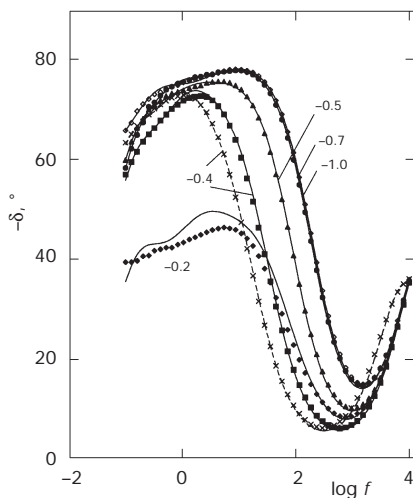


FIG. 4

Dependence of the phase angle δ on ac frequency f (in Hz) for the interface Bi(001)|LiCl (concentration c) in ethanol (points, experimental data; solid lines, fitting results for $c = 0.1 \text{ mol l}^{-1}$; dashed line, fitting result for $c = 0.02 \text{ mol l}^{-1}$). The electrode potential E , V (vs SCE) is given

and

$$C(\omega) = \{j\omega[Z(\omega) - R_s]\}^{-1} = C_1 + C_2/(1 + (\sigma_{ad}C_2\sqrt{j\omega}). \quad (2)$$

In Eqs (1) and (2) and in Fig. 5, R_s is the electrolyte resistance, C_1 is an interfacial capacitance as frequency $f \rightarrow \infty$ (so-called high-frequency or “true” capacitance), $C_2 = C_0 - C_1$ is the adsorption capacitance, related by the dependence of Gibbs adsorption Γ on E and defined as $C_2 = (\partial\sigma/\partial\Gamma)_E(\partial\Gamma/\partial E)_\mu$, where σ is surface charge density and μ is the chemical potential, C_0 is the low-frequency capacitance, defined at $f \rightarrow 0$ as $C_0 = (\partial\sigma/\partial E)_{\Gamma,\mu} + (\partial\sigma/\partial\Gamma)_E \times (\partial\Gamma/\partial E)_\mu$ and $C_1 = (\partial\sigma/\partial E)_{\Gamma,\mu}$, W_1 is the Warburg-like diffusion impedance, caused by slow diffusion of the particles to the electrode surface with Warburg constant $\sigma_{ad} = \tau_D^{1/2}/C_2$, where τ_D is the diffusion-controlled relaxation time $\tau_D = 1/2\pi f_D$. The presence of the Warburg-like impedance in the absence of significant adsorption was explained by slower diffusion of solvated ions in alcohols¹⁶. The Warburg diffusional impedance Z_W can be simulated by the generalised finite Warburg element for a short circuit terminus model, expressed as²²

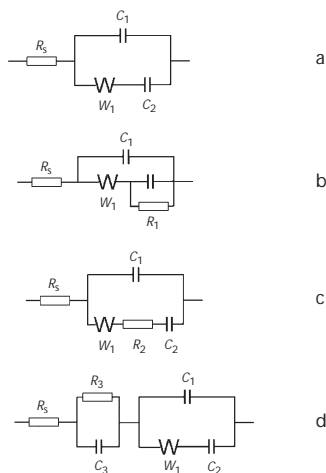


FIG. 5

Equivalent circuits of an electrode used. Description of equivalent circuits: R_s , solution resistance; R_1 , faradaic process resistance; R_2 , adsorption resistance; R_3 , diffuse layer resistance; C_1 , “true” double layer capacitance; C_2 , adsorption capacitance; C_3 , diffuse layer capacitance; W_1 , Warburg-like diffusion impedance

$$Z_W = R_D \tanh [(jT\omega)^{\alpha_w}] / (jT\omega)^{\alpha_w}, \quad (3)$$

where R_D is the limiting diffusion resistance, $T = L^2/D$, where L is the effective diffuse layer thickness and D is the effective diffusion coefficient of the particles, α_w is a fractional exponent varying between 0 and 1. It is to be noted that for the semi-infinite diffusion models that would be valid in the case of adsorption of ions, $\alpha_w = 0.5$.

Analysing the impedance spectra obtained by us for the Bi(*hkl*)|LiI systems in ethanol²³, it was found that in the potential region, where the adsorption of I^- ions can be regarded as nearly physical ($E \leq -0.6$ V), the Frumkin–Melik-Gaikazyan model also described the experimental data quite well. At more positive potentials, however, the fitting of experimental results to EC (see Fig. 5a) failed or led to parameters that were physically unrealistic or had very high relative errors. So, a more complicated EC (see Fig. 5b) was introduced, including a resistor R_1 parallel to capacitance C_1 . This means that a parallel process of the charge transfer, most probably the partial charge transfer from I^- ions to Bi(*hkl*) occurs²³. For the present system Bi(001)|LiCl circuit EC (see Fig. 5a) can be used up to $E = -0.3$ V and only at $E > -0.3$ V addition of the resistor R_1 is necessary. It must be noted that at $E \geq -0.2$ V, the oxidation of the electrode surface begins. Thus, in almost the whole region of potentials studied, the Cl^- ions retain their charge and, as a first approximation, adsorption can be regarded as a physical adsorption. This means that the classic methods for calculation of the extent and parameters of adsorption are applicable to Cl^- anions at the Bi(001)|ethanol interface.

For some systems it has been found^{18,24} that for a better fit it is necessary to add a resistor corresponding to adsorption resistance, R_2 , in series to W_1 and C_2 (EC in Fig. 5c), thus leading to the model first introduced by Ershler²⁵. Replacement of C_1 in ECs (see Fig. 5a or 5c) with a constant-phase element (CPE) is also a common procedure²⁴. In the present case, however, analogously to the LiI–ethanol system²³, no improvement of the fit was obtained using EC (see Fig. 5c) or introducing a CPE. In the former case, the fitting led to very large relative errors of R_2 and no decrease of χ^2 values. The use of CPE led to only slight improvement of fitting and caused the values of α_w to decline substantially from 0.5, which should not be expected for the present system. Attempts to predefine $\alpha_w = 0.5$ in this case led to failure of the fitting process.

It can be seen in Fig. 2 that a small half-circle forms at the high-frequency part of impedance spectra ($f > 1.2$ kHz at 0.1 mol l^{-1}). This part of

spectra most probably describes the electrolyte bulk properties in the diffuse layer and can be simulated only if a capacitance and resistance in parallel are added to EC (see Fig. 5a), yielding EC (see Fig. 5d). In this EC the capacitance and resistance C_3 and R_3 mainly represent the diffuse layer characteristics. It should be noted that there was no significant difference between the values of basic parameters (C_1 , C_2 , components of W_1), obtained by fitting with and without the elements C_3 and R_3 in ECs. So, as the diffuse layer parameters are not of interest in the present case, the high-frequency part can be left out from fitting procedure (analogously to the $\text{LiClO}_4|\text{ethanol}$ system¹⁶).

The solid lines in Figs 2–4 illustrate the fitting results using EC (see Fig. 5d). As can be seen from Figs 2–4, the calculated curves describe the experimental data quite well in the whole range of electrode potentials except at $E = -0.2$ V, where surface oxidation process begins. This conclusion is supported also by small values of the χ^2 function in Table I. As follows from Table I, the α_w values are close to 0.5 in the whole range of measured potentials, *i.e.*, the systems studied can be described by the semi-infinite diffusion model. So, predefining $\alpha_w = 0.5$ or letting α_w values free, the course of fitting practically does not change the values of other parameters.

TABLE I
Results of non-linear least-squares fitting for $\text{Bi}(001)|\text{LiCl}$ system in ethanol

Parameter	E , V	c , mol l ⁻¹		
		0.1	0.02	0.003
$\chi^2 \times 10^3$	-0.9	1.4	1.3	0.9
	-0.5	0.8	0.7	0.7
	-0.2	3.0	0.9	0.5
α_w	-0.9	0.51 ± 0.03	0.50 ± 0.03	0.47 ± 0.03
	-0.5	0.50 ± 0.02	0.49 ± 0.02	0.48 ± 0.02
	-0.2	0.46 ± 0.06	0.48 ± 0.02	0.49 ± 0.02
R_D , $\Omega \text{ cm}^2$	-0.9	$1.0 \times 10^5 \pm 1 \times 10^4$	$2.0 \times 10^5 \pm 3 \times 10^4$	$3.6 \times 10^5 \pm 2 \times 10^4$
	-0.5	$1.6 \times 10^4 \pm 1600$	$6.9 \times 10^4 \pm 8500$	$1.5 \times 10^5 \pm 9000$
	-0.2	2400 ± 200	3600 ± 300	4700 ± 600

Figures 6 and 7 demonstrate the dependences of capacitances C_1 and C_2 , obtained by fitting using EC (see Fig. 5b), on the electrode potential. It should be noted that no well-defined dependence of the Warburg imped-

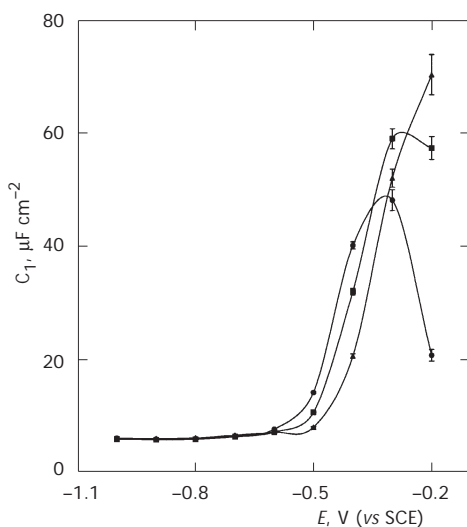


FIG. 6
Dependence of "true" double layer capacity C_1 on E for the Bi(001) plane in 0.1 (●), 0.02 (■) and 0.003 M (▲) LiCl solutions in ethanol

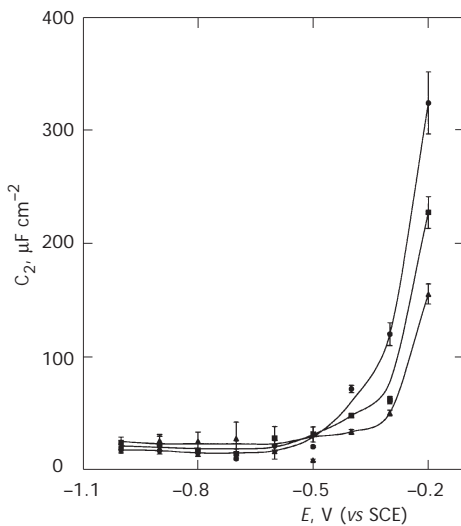


FIG. 7
Dependence of adsorption capacity C_2 on E for the Bi(001) plane in 0.1 (●), 0.02 (■) and 0.003 M (▲) LiCl solutions in ethanol

ance parameters (R_D , α_w , T) on E was found. Because of that the values of these parameters were not plotted, but are presented at some fixed E in Table I together with the χ^2 values. It follows from Table I that the χ^2 values are about the same order as for the $\text{LiClO}_4|\text{ethanol}$ system¹⁶. It can be also seen that diffusion resistance R_D decreases when E becomes more positive and concentration of the solution increases.

As can be seen from Fig. 6, the "true" double layer capacitance C_1 obtained at $f \rightarrow \infty$ increases in the region where the adsorption of Cl^- ions occur and a maximum appears at $E = -0.3$ V in decimolar solution, corresponding to the maximum on the experimental C - E curve (Fig. 1). In more dilute solutions, this maximum disappears. The adsorption capacitance increases monotonically in the same direction, reflecting the increase in the Cl^- ions adsorption on the $\text{Bi}(001)$ plane. Values of R_1 , characterising the rate of charge transfer, are high (10^6 - 10^{10} Ω) in almost the whole range of Cl^- adsorption but diminish sharply to 10^4 Ω at -0.2 - -0.3 V indicating the possibility that at these potentials the mechanism of the adsorption becomes similar to that of Γ ions, *i.e.*, that the charge transfer from ions to metal begins.

Adsorption Characteristics of Cl⁻ Ions

As the first step in calculation of the surface excess values for adsorbed Cl^- anions, the C - E curve for 0.1 M LiClO_4 solution was integrated to determine 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 Bi single crystal planes in ethanol were estimated earlier²⁶. For solutions containing chloride ions, σ values were obtained by back integration from $E = -1.4$ V, where the C - E curves coincide and the adsorption of Cl^- ions is negligible.

The following calculations of adsorption characteristics were performed similarly to those for the other non-aqueous systems, for both σ and E as the independent electric variables. First, the $\Delta\sigma = \sigma_0 - \sigma$ values at constant E were calculated (σ_0 is the 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 $\Delta\gamma = \gamma_0 - \gamma$ and $\gamma_0 - \gamma$ are the specific surface work values in the supporting electrolyte and in the solution containing Cl^- , respectively. After that, the values of Parsons' function $\xi = \gamma + \sigma E$ and $\Delta\xi = \xi_0 - \xi$ were calculated. The charge due to specific adsorption of the Cl^- ions σ_1 was calculated according to the mixed electrolytes method²⁷

$$\sigma_1 = (F/RT)(\partial\Delta\xi/\partial \ln x)_{\sigma=\text{const}} \quad (4)$$

$$\sigma_1 = (F/RT)(\partial\Delta\gamma/\partial \ln x)_{E=\text{const}} \quad (5)$$

It was found, that independently of the chosen electric variable, practically the same σ_1 values were obtained at corresponding σ and E values, which can be regarded as an evidence of the correctness of the experimental data. In Fig. 8, the σ_1 - E curves of the Bi(001) plane at three different LiCl concentrations in ethanol, and, for comparison, in methanol¹⁰ and propan-2-ol³, are shown. As can be seen in Fig. 8, the adsorption activity of Cl^- in ethanol is remarkably higher than in methanol but approximately to the same extent lower than in propan-2-ol.

To find the Gibbs energy of adsorption $-\Delta G_A$, the σ_1 values for all planes studied were fitted to the simple virial isotherm

$$\ln(\sigma_1/zxc) = -\Delta G_A/RT - 2B\sigma_1, \quad (6)$$

where z is the charge number of adsorbed anion ($z = -1$ in the present case), c is the total concentration of solution (0.1 mol l^{-1}) and B is the second

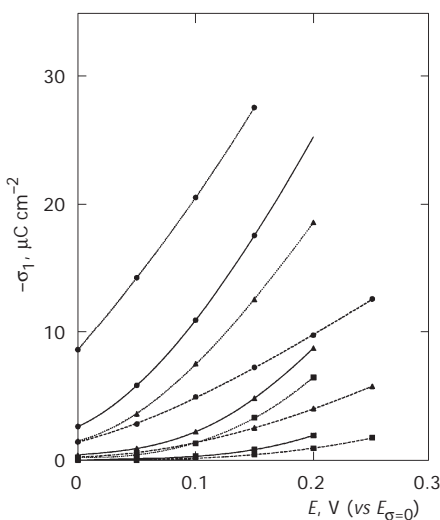


FIG. 8

Plot of the charge σ_1 due to specifically adsorbed Cl^- anions against electrode potential E in ethanol (solid lines), methanol (dashed lines) and propan-2-ol (dotted lines) on Bi(001) electrode at $x = 1$ (●), 0.1 (▲) and 0.01 (■)

virial coefficient, characterising the mutual repulsion and size of the adsorbed ions. Like for other systems studied³⁻¹⁰, the plots of $\ln(-\sigma_1/xc)$ versus σ_1 are linear both for $E = \text{const}$ and for $\sigma = \text{const}$. This is demonstrated in Figs 9 and 10, where the corresponding plots for the Bi(001) plane are shown.

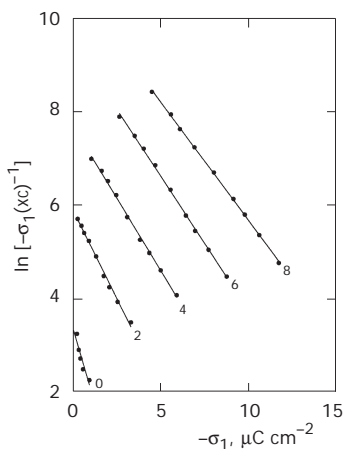


FIG. 9

Plot of the function $\ln(-\sigma_1/xc)$ against the charge σ_1 of specifically adsorbed Cl^- anions at the Bi(001)|ethanol interface. The electrode charge σ , $\mu\text{C cm}^{-2}$ is given

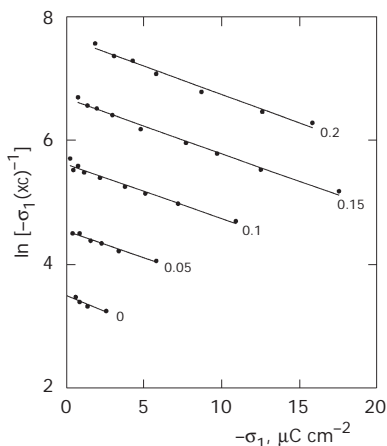


FIG. 10

Plot of the function $\ln(-\sigma_1/xc)$ against the charge σ_1 of specifically adsorbed Cl^- anions at the Bi(001)|ethanol interface. The electrode potential E , V (vs $E_{\sigma=0}$) is given

According to Eq. (6), the extrapolation of the straight lines in Figs 9 and 10 to the condition $\sigma_1 = 0$ yields $-\Delta G_A$ for given electrode charge or potential. The $-\Delta G_A$ values were calculated using the common standard conditions (1 ion cm^{-2} on the electrode surface and 1 mol l^{-1} of ions in the bulk of solution). The $-\Delta G_A-E$ and $-\Delta G_A-\sigma$ plots for the present system are both linear. The $-\Delta G_A^0$ values at $\sigma = 0$ and at $E = E_{\sigma=0}$ for the adsorption of Cl^- ions are presented in Table II. As it was shown²⁸, $-\Delta G_A^0$ is a good characteristic for the comparison of the adsorption of ions in various solvents and on various surfaces as this value at $\sigma = 0$ is independent of c and the $-\Delta G_A^0$ values are the same for different modifications of virial isotherms. As follows from Table II, there are no differences between the $-\Delta G_A^0$ values for uncharged electrode surface obtained at different electric variables. It is also seen that the $-\Delta G_A^0$ value for Cl^- is significantly less than the corresponding $-\Delta G_A^0$ values for the Br^- and I^- anions^{5,9}. Comparing the data for different solvents, it can be seen that like the charge of specific adsorption (Fig. 6) the $-\Delta G_A^0$ value for Cl^- adsorption is higher in ethanol than in methanol but the $-\Delta G_A^0$ is lower than in propan-2-ol^{3,4}. However, the differences for Cl^- anions are lower than for the case of iodide anions⁹.

The obtained adsorption data were used for the calculation of the electro-sorption valency (formal charge transfer coefficient²⁹) values γ from the formula³⁰

$$\gamma = (1/F)(\partial\Delta G_A/\partial E)_\Gamma = -(1/F)(\partial\sigma/\partial\Gamma)_E, \quad (7)$$

TABLE II

The standard Gibbs energy of adsorption of Cl^- ions on the uncharged Bi(001) electrode in ethanol

Condition	$-\Delta G_A^0$, kJ mol^{-1}		
	ethanol	methanol	propan-2-ol
$E = E_{\sigma=0}$	82.2	81.4	85.3
$\sigma = 0$	82.0	81.3	84.8

where Γ is the surface excess of adsorbed ions ($\Gamma = \sigma_1/zF$). Following Eq. (7), γ was calculated in two different ways. First, as the $-\Delta G_A-E$ plot was linear, γ can be regarded as constant and calculated from the slope of this plot, leading to $\gamma = 0.53$. Second, the $\sigma-\sigma_1$ plots at constant E were constructed and the slope values of these plots were found (according to the second part of Eq. (7)). The $\sigma-\sigma_1$ plot for the adsorption of Cl^- ions on $\text{Bi}(001)$ plane is straight line as can be seen in Fig. 11. It follows from Fig. 11 that the lines are nearly parallel with the slope value 0.52 confirming the constancy of γ for the present system. Therefore, both methods yield practically the same value for γ .

To characterise the inner layer properties in the case of Cl^- ions adsorption on the $\text{Bi}(001)$ single crystal plane the values of the surface dipole μ_s , created by an adsorbed anion and its image charge in the metal^{31,32}, were calculated from Eq. (8)

$$\mu_s = ze_0\varepsilon(1 - \gamma/z)/K_{02}, \quad (8)$$

where e_0 is the elementary charge, ε is the dielectric permittivity and K_{02} is the inner layer integral capacitance.

The calculation of capacitance K_{02} for Cl^- ion adsorption is more complicated than for I^- and Br^- ions because of the coadsorption of ClO_4^- ions¹¹.

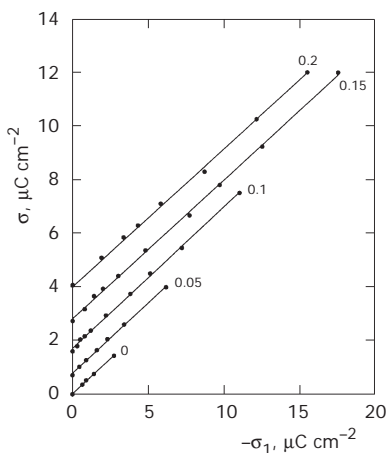


FIG. 11

Plot of the electrode charge σ against the charge σ_1 of specifically adsorbed Cl^- anions at the $\text{Bi}(001)|\text{ethanol}$ interface. The electrode potential E , V (vs $E_{\sigma=0}$) is given

However, it was found for both Bi polycrystal³³ and single crystal planes^{3,7} that in the same alcohol K_{02} practically does not depend on the nature of the anion. Therefore the K_{02} values, found in our previous work⁵ for the Br^- ions, can be used for the present system. The permittivity of the inner layer ϵ was taken equal to that of vacuum ($8.85 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$, ref.³⁰). Using these approximations, the μ_s value obtained at $\sigma = 0$ is $3.5 \times 10^{-30} \text{ C m}$ and, in the region where the adsorption of Cl^- ions is significant, $\mu_s = 2.9 \times 10^{-30} \text{ C m}$. Similar for other systems studied, μ_s value for the Cl^- anions, adsorbed on Bi(001) from ethanol, is much smaller than the value calculated for a dipole formed by a charged ideal sphere of an ionic radius r_i ($r_{\text{Cl}^-} = 0.181 \text{ nm}$) adsorbed at the perfect conductor (for Cl^- $\mu_s = 29.0 \times 10^{-30} \text{ C m}$ or $\mu_s = 8.69 \text{ D}$) ($1 \text{ D} = 3.336 \times 10^{-30} \text{ C m}$). The low values of μ_s show that a dipole formed by an adsorbed chloride ion and its image charge in the metal is significantly screened by the solvent molecules and metal electrons.

CONCLUSIONS

The impedance measurements indicated that the Bi(001) single crystal plane in LiCl solutions in ethanol is stable in the range of potentials at least $-1.6 < E < -0.2 \text{ V}$ (vs SCE). At $E > -0.2 \text{ V}$ (SCE), a rapid increase in faradaic current was detected. The analysis of the impedance spectra was performed by fitting the experimental data to various equivalent circuits. The dependences of "true" capacitance, adsorption capacitance and diffusion resistance on the electrode potential have been obtained. It was found that almost in the whole potential region where the adsorption of Cl^- ions occurs, the behaviour of Cl^- ions at Bi(001)|ethanol interface can be well described using the classic Frumkin-Melik-Gaikazyan model and only at $E > -0.3 \text{ V}$, a more complicated equivalent circuit should be used for fitting the experimental impedance spectra. It is therefore possible that at $E > -0.3 \text{ V}$ (SCE) the partial charge transfer from the Cl^- ions to the Bi surface atoms takes place and the formation of the surface compound is probable. The adsorption characteristics of the Cl^- ions on the Bi(001) plane can thus be obtained using the traditional calculation methods.

It was found that the adsorption characteristics of the Cl^- anions on the Bi(001) single crystal plane in ethanolic solutions are close at different electric variables, indicating that there were no significant systematic errors in obtaining and handling the experimental data. It was also found that the charge of specifically adsorbed Cl^- ions as well as the Gibbs energy of adsorption for the Bi(001)|ethanol interface increases in the order of solvents methanol < ethanol < propan-2-ol, reflecting the decrease in the solvation

energy of Cl^- ions in the same order. The electrosorption valency obtained for the present system was found to be independent of the electrode potential. The very low values of the dipole moment formed by adsorbed chloride ion and its image charge show that the dipole is significantly screened by the solvent molecules and metal electrons. Although the main reason for the low values of the surface dipole is probably the screening of this dipole by the "free" electrons in the metal, the role of the solvent molecules should also be considered as important.

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