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Adsorption of 1-heptanol on bismuth single-crystal plane electrodes

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Abstract Cyclic voltammetry, impedance and chronocoulometry have been employed for the quantitative study of 1-heptanol (1-HepOH) adsorption on the bismuth single-crystal plane|aqueous Na_2SO_4 solution interface. The adsorption isotherms, Gibbs energies of adsorption, ΔG_A° , the limiting surface excess, Γ_{max} , and other adsorption parameters have been determined. The adsorption of 1-HepOH on Bi single-crystal planes is mainly physical and is limited by the rate of diffusion of organic molecules to the electrode surface. Comparison of the adsorption data for 1-HepOH with other alcohols shows that the adsorption characteristics depend on the structure of the hydrocarbon chain. The adsorption activity of adsorbates at the bismuth|solution interface increases in the sequence 1-propanol < 1-butanol < 1-pentanol < 1-hexanol < 1-heptanol as the adsorption activity at the air|solution interface increases. For all the compounds studied, the adsorption activity increases in the sequence of planes as $(111) < (001) < (01\bar{1})$.

Keywords Cyclic voltammetry · Impedance · Chronocoulometry · 1-Heptanol · Bismuth single crystal

Introduction

This work is a part of the project devoted to the study of the influence of the crystallographic structure of bismuth on the adsorption of neutral organic molecules at the

Bi|solution interface [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19]. Statistical treatment of electron diffraction studies and capacitance data shows that the surface of the Bi solid drop electrode (BDE) consists mainly (ca. 60%) of homogeneous segments whose crystallographic, double layer and adsorption characteristics are similar to those for the (001) plane of bismuth [17, 18].

The chemical nature and crystallographic structure of the single-crystal plane electrode is known to affect the structuring of interfacial water molecules, which has been studied extensively from both experimental and theoretical points of view [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32]. Systematic adsorption measurements of linear 1-aliphatic alcohols and their isomers from aqueous electrolyte solutions have been carried out on various sp metals, such as Hg, Pb, Bi, Cd, Sn, Sb, Zn, In-Tl and Tl [13, 14, 15, 16, 17, 22, 23, 24, 25, 26, 27, 28, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43]. In general, these measurements indicate that the adsorption of aliphatic compounds is weaker the more hydrophilic is the metal. Comparison of the adsorption data for 1-propanol (1-PrOH), 1-butanol (1-BuOH), cyclohexanol (CyOH), 1-pentanol (1-PenOH) and 1-hexanol (1-HexOH) shows that the difference of the adsorption parameters for various planes increases as the adsorption activity of adsorbate at the air|solution interface, as well as at the electrode|electrolyte solution interface, rises [10, 39, 40, 44, 45, 46]. This is mainly caused by the fact that with decreasing the molar volume of adsorbate the transformations in the adsorption layer structure, caused by the adsorption of one surfactant molecule, decrease in comparison with the situation when the adsorption of very large particles takes place. The adsorption studies of various butanol isomers [8] shows that the adsorption parameters depend on the geometrical structure of the hydrocarbon tail of the adsorbate, and thus comparison of the adsorption behaviour of 1-HepOH with CyOH and 1-HexOH should provide more information on the influence of the hydrocarbon chain structure on

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the adsorption process and about the attractive interactions in the adsorbed layer.

For a more profound understanding of the importance of the crystallographic structure of the electrode surface and the geometrical structure of the hydrocarbon chains of adsorbate in the adsorption phenomena, in the present work we investigated the adsorption of 1-heptanol (1-HepOH) on singular (111), (001) and (011) faces of bismuth and compared the parameters obtained with the adsorption data of various organic compounds on Bi planes [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12].

Experimental

The experimental procedure used in this work has been described previously [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12]. The electrode surface was electrochemically polished in aqueous KI+HCl solution at a current density $i \leq 1.5 \text{ A cm}^{-2}$. Thereafter, the second X-ray diagram was used to determine the precise angle, and only the samples whose precision on the orientation was better than $\pm 0.10^\circ$ were used for electrochemical investigations. After electrochemical polishing, the electrodes were very well rinsed with ultra-purified water and were polarized at -1.0 V versus a saturated calomel electrode (SCE) in the working surface-inactive solution during 1–1.5 h.

For an additional characterization of the working surface of the electrodes, electron microscopic analysis by a JEOL-JSM-35CF (20,000 \times max.) and the AFM method have been used. According to these measurements, the electrochemically polished surfaces of the bismuth electrodes were very smooth [7, 44].

Water for preparing the solutions was treated with the Milli Q+ purification system. Solutions were prepared volumetrically using Na_2SO_4 purified by triple recrystallization from water, and heated in vacuum to dryness. Na_2SO_4 was calcined at 700°C immediately prior to the measurements. Electrolytic hydrogen was bubbled for 1–2 h through the electrolyte before the submersion of the electrode into the solution and the temperature was kept at 298 K . 1-HepOH was purified according to Weissberger [47].

Results and discussion

Cyclic voltammograms

The cyclic voltammograms (CVs) were recorded in order to determine the quality of the surfaces investigated and the potential range in which the adsorption of 1-HepOH occurred. The shape of the CV recorded for the supporting electrolyte was characteristic of the bismuth single crystal [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12] and the electrodes investigated were ideally polarizable in the potential range of -1.7 to -0.4 V (SCE) in aqueous $0.05 \text{ M Na}_2\text{SO}_4$ solution.

Differential capacitance versus potential curves (C - E curves)

The electrical double layer (edl) differential admittance was measured at ac frequencies ν from 0.1 to $21,000 \text{ Hz}$ (Figs. 1 and 2). The capacitance dispersion with ν is small in the proximity of the differential capacitance

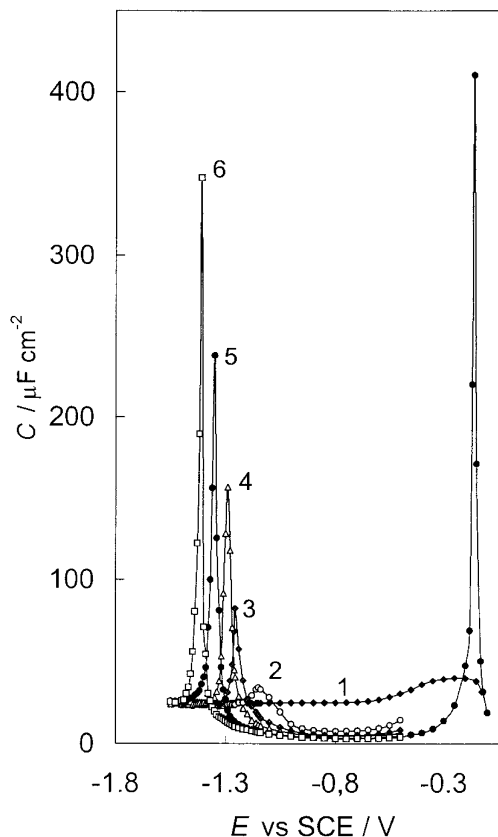


Fig. 1 C vs. E curves ($\omega = 0$) for Bi(111) in $0.05 \text{ M Na}_2\text{SO}_4$ (I) and with addition of 1-HepOH (M): 0.001 (2); 0.002 (3); 0.003 (4); 0.006 (5); 0.0075 (6)

minimum (in the region of maximum adsorption), whereas it increases noticeably in the region of the adsorption-desorption peaks. Comparison of the ($C^{\text{peak}} - C_0$) versus $\omega^{1/2}$ curves (C^{peak} = differential capacitance at the potential of the adsorption-desorption maximum E^{peak} ; C_0 = differential capacitance at E^{peak} in the base electrolyte; $\omega = 2\pi\nu$) for 1-PrOH, 1-BuOH, CyOH, 1-PenOH, 1-HexOH and 1-HepOH shows that this dependence increases with the rise of molecular weight and the molar volume of the adsorbate. As shown elsewhere [27, 48], if the rate of adsorption of organic compounds is limited by diffusion, the equilibrium values of the differential capacitance at $\nu = 0$ can usually be found with a sufficient degree of accuracy by extrapolation of the $C_{\text{add}}(\omega^{1/2})$ curve to $\omega^{1/2} = 0$. According to the experimental results (Fig. 3), in the region of $0.1 < \nu < 30 \text{ Hz}$ the $C_{\text{add}}(\omega^{1/2})$ curves have a good linearity and, accordingly, we can obtain the equilibrium values of differential capacitance using the extrapolation method [27, 48].

According to the method described elsewhere [27, 48, 49, 50], the equilibrium values of the differential capacitance can be calculated by Eq. (1):

$$C_{\text{add}}(\omega = 0) = \frac{\{C_{\text{add}}^2(\omega)R_p^2(\omega)\omega^2 + 1\}}{\{[C_{\text{add}}(\omega)R_p(\omega)\omega - 1]R_p(\omega)\omega\}} \quad (1)$$

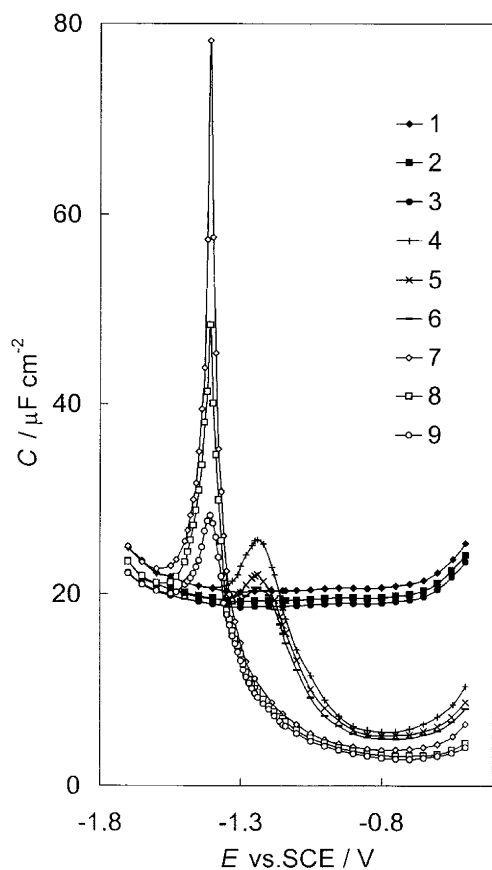
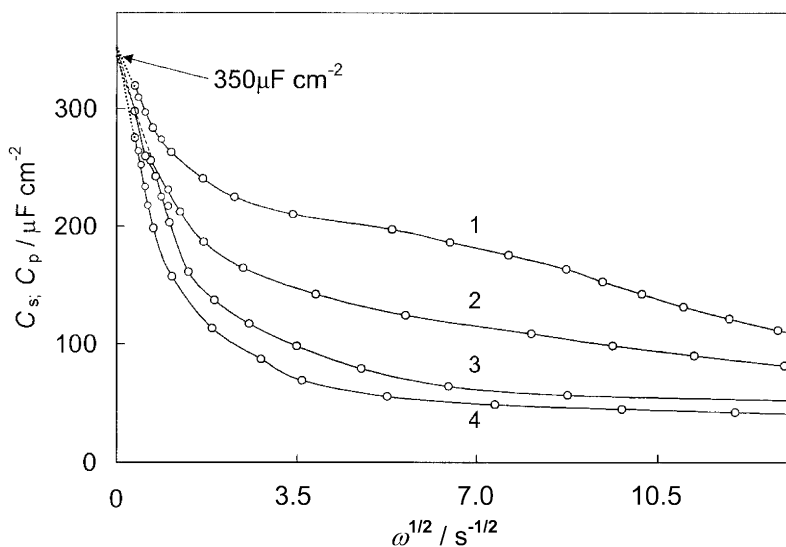


Fig. 2 C vs. E curves for Bi(111) in 0.05 M Na_2SO_4 (1, 2, 3) and with addition of 0.002 M 1-HepOH (4, 5, 6) and 0.0075 M 1-HepOH (7, 8, 9) at different frequencies: 21 Hz (1, 4, 7); 210 Hz (2, 5, 8); 2100 Hz (3, 6, 9)

where $C_{\text{add}}(\omega)$ and $R_p(\omega)$ are the values of differential (additional) capacitance and parallel resistance at $\omega = \text{const.}$ The components of the adsorption impedance were calculated from the impedance data of the cell used for the measurements (series circuit), i.e. $C_s(\omega)$ and

Fig. 3 C_s vs. $\omega^{1/2}$ (1, 3) and C_p vs. $\omega^{1/2}$ (2, 4) curves for Bi(011) (1, 2) and Bi(001) (3, 4) at the potential of the adsorption-desorption peak, E^{peak} , in 0.05 M Na_2SO_4 with addition of 0.007 M 1-HepOH



$R_s(\omega)$, following described procedures [27, 48, 49, 50]. By extrapolating the $R_s(\omega)$ values to $\omega \rightarrow \infty$ the solution resistance $R_s(\omega) = R_{\text{sol}}$ was determined. Since the amount of organic compounds added is small and does not affect the solution resistance, one can assume R_{sol} to be equal to the ohmic component R_s of the impedance in the pure base electrolyte solution. The values of R_{sol} and R_s obtained in this work are in good agreement with previous data [8, 51]. Then the series equivalents $R_s(\omega) - R_{\text{sol}}$ and $C_s(\omega)$ of the impedance were converted into the parallel equivalents $C_p + C_{\text{true}}$ and R_p using known relations [27, 48, 49, 50]. According to the data in Fig. 3, the C_s vs. $\omega^{1/2}$ and C_p vs. $\omega^{1/2}$ curves coincide at $\omega \rightarrow 0$ and thus the diffusion stage of 1-HepOH molecules to the Bi surface is the rate-determining process of adsorption in the region of the adsorption-desorption peaks.

All the C - E curves determined in the presence of 1-HepOH in the solutions investigated merge with the curve for the supporting electrolyte at -1.7 V (SCE) (Fig. 1), indicating that 1-HepOH molecules are completely desorbed from the bismuth surface at these negative potentials. At less negative potentials the C - E curves display the characteristic adsorption-desorption peaks. The height of the peak increases and its potential shifts to the negative direction with increasing 1-HepOH concentration. As we can see from Fig. 1 and from comparison of data for 1-HepOH with other aliphatic compounds, the shape (the height and width) of the adsorption-desorption maximum at $c_{\text{org}} = \text{const.}$ and $\omega = \text{const.}$ depends on the geometrical structure of the adsorbate hydrocarbon chains. At $E < E_{\sigma=0}$ the attractive interaction constant a^{peak} obtained according to the Frumkin-Damaskin theory [27, 30] increases in the sequence of compounds as 1-PrOH < 1-BuOH < 1-PenOH < 1-HexOH < 1-HepOH < CyOH as the molar volume of adsorbate rises, except CyOH. The potential of the adsorption-desorption maximum E^{peak} at $E < E_{\sigma=0}$ ($c_{\text{org}} = \text{const.}$) depends on the geometrical

structure of the adsorbate, and the adsorption activity of adsorbates increases in the sequence of 1-PrOH to 1-HepOH (Fig. 4). The height and potential of the adsorption-desorption peaks depend on the geometrical structure of the electrode surface. According to the experimental data, these maxima increase in height in the sequence of faces as $(01\bar{1}) < (111) \leq (001)$. Accordingly, the attractive interaction constant a^{peak} at E^{peak} increases as the superficial density of the atoms decreases. The same tendency is valid for 1-PrOH, 1-BuOH, CyOH, 1-PenOH and 1-HexOH adsorption at the Bi single-crystal plane electrodes [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12].

At $E \approx E_{\sigma=0}$ the differential capacity decreases to a value much smaller than that observed for the pure base electrolyte. The potentials of the capacity maximum in the C - E curves, E_{max} , are independent of the concentration of adsorbate, indicating that the orientation of adsorbed 1-HepOH molecules is practically independent of the surface coverage θ in the region of maximum adsorption. The values of the limiting capacitance C_1 at the surface coverage $\theta = 1$ at $E = E_{\text{max}}$, obtained by the extrapolation of the linear dependence of $1/C$ on $1/c_{\text{org}}$ to $1/c_{\text{org}} = 0$ (c_{org} = concentration of organic compound in solution), are practically independent of plane studied; however, a very small increase of C_1 seems to take place in the order $(001) \leq (01\overline{1}) \leq (111)$ (Table 1). According to the Helmholtz equation for the plate condenser, $C = \epsilon\epsilon_0/d$ (where ϵ and ϵ_0 are the dielectric constants of the medium and vacuum, respectively, and d is the thickness of the adsorbed layer), the decrease of C_1 can be explained by the decrease of ϵ caused by the increase of the amount of

organic compound in the adsorbed layer, as well as by the increase of the adsorbed layer thickness, which may be caused by the more vertical orientation of the adsorbed molecules.

The adsorption-desorption maxima at $E^{\text{peak}} > E_{\sigma=0}$ for 1-HepOH were found at $-0.4 < E < -0.15$ V (SCE). For more concentrated solutions of 1-HepOH ($c_{\text{org}} > 0.005$ M), the peaks lie at very positive potentials [$E > -0.25$ V (SCE)] and are probably distorted by a slight specific co-adsorption of the anions [3, 4, 5, 6, 7, 8, 9, 10]; therefore, they were not used for the calculation of the adsorption parameters. As in the region of potentials $E^{\text{peak}} < E_{\sigma=0}$, the heights of the peaks at $E^{\text{peak}} > E_{\sigma=0}$ increase in the order of planes as $(01\bar{1}) < (111) \leq (001)$, but the maxima at $E^{\text{peak}} > E_{\sigma=0}$ are noticeably narrower than those at $E < E_{\sigma=0}$. Thus, the attractive interaction at $E > E_{\sigma=0}$ is somewhat higher than that for a negatively charged surface.

Charge density vs. potential (σ - E) curves

At first, the charge density-potential curves for solutions with different 1-HepOH additions were obtained by the back integration of the C - E curves (extrapolated to $\omega = 0$), starting from $E = -1.7$ V (SCE) and assigning the value of $\sigma(E = -1.7$ V) equal to $\sigma_0(E = -1.7$ V), because there is no adsorption at $E = -1.7$ V (SCE). The shape of σ - E curves is typical of the behaviour observed for the adsorption of neutral organic molecules at ideally polarizable electrodes, but the potential at which the σ - E curves for different $c_{1\text{-HepOH}}$ intersect the σ_0 - E curve is noticeably more negative (~ 100 – 200 mV) than the

Fig. 4 Dependence of the difference between the potential of the adsorption-desorption maximum and the zero charge potential ($E^{\text{peak}} - E_{\sigma=0}$) on $\log c_{\text{org}}$ at Bi(111) for various organic compounds: 1-HepOH (1); 1-HexOH (2); 1-PenOH (3); CyOH (4); 1-BuOH (5); 1-PrOH (6)

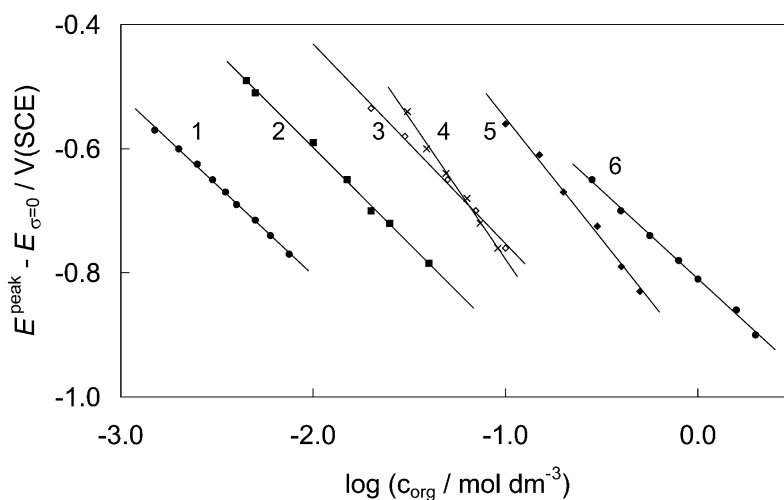


Table 1 Adsorption parameters for 1-heptanol on Bi single-crystal planes (impedance data at $\omega = 0$)

Plane	$a_m \pm 0.1$	$C_1 \pm 0.05$ ($\mu\text{F cm}^{-2}$)	$10^{10} \Gamma_{\text{max}} \pm 0.3$ (mol cm^{-2})	$S_{\text{max}} \pm 0.02$ (nm^{-2})	$B_m \pm 20$ ($\text{dm}^3 \text{cm}^{-2}$)	$-\Delta G_{\text{ads}}^\circ \pm 0.3$ (kJ mol^{-1})
(111)	1.45	2.5	4.4	0.38	350	24.5
(001)	1.22	2.3	5.0	0.33	608	25.8
(01 $\bar{1}$)	1.16	2.4	3.1	0.53	1060	27.2

potential of maximum adsorption E_{\max} , obtained from $[C(\omega=0)-C_0(\omega=0)]-E$ curves according to the method described elsewhere [27, 30]. This behaviour is typical for organic compounds with a high molecular weight and with a noticeable chemical interaction of adsorbate molecules with surface atoms, whose adsorption is limited by the rate of diffusion of adsorbate to the electrode surface, as well as by the rate of the partial charge transfer between metal and adsorbate [17, 18, 19]. Thus, in spite of the extrapolation of $C-E$ curves to $\omega \rightarrow 0$, the $C-E$ curves in the region of the adsorption-desorption peaks are somewhat non-equilibrium and the integration of $C-E$ curves gives erratic $\sigma-E$ curves in the region $E < E^{\text{peak}}$ if we use the back-integration method. For that reason the $\sigma-E$ curves (Fig. 5a), used for calculations of the adsorption parameters, were obtained by the integration of $C-E$ curves extrapolated to the condition $\omega=0$, starting from the values of potential E_{\min}^{org} , corresponding to the zero charge potential of the system consisting of the dilute base electrolyte solution (0.001 M Na_2SO_4) with addition of x M 1-HepOH [12].

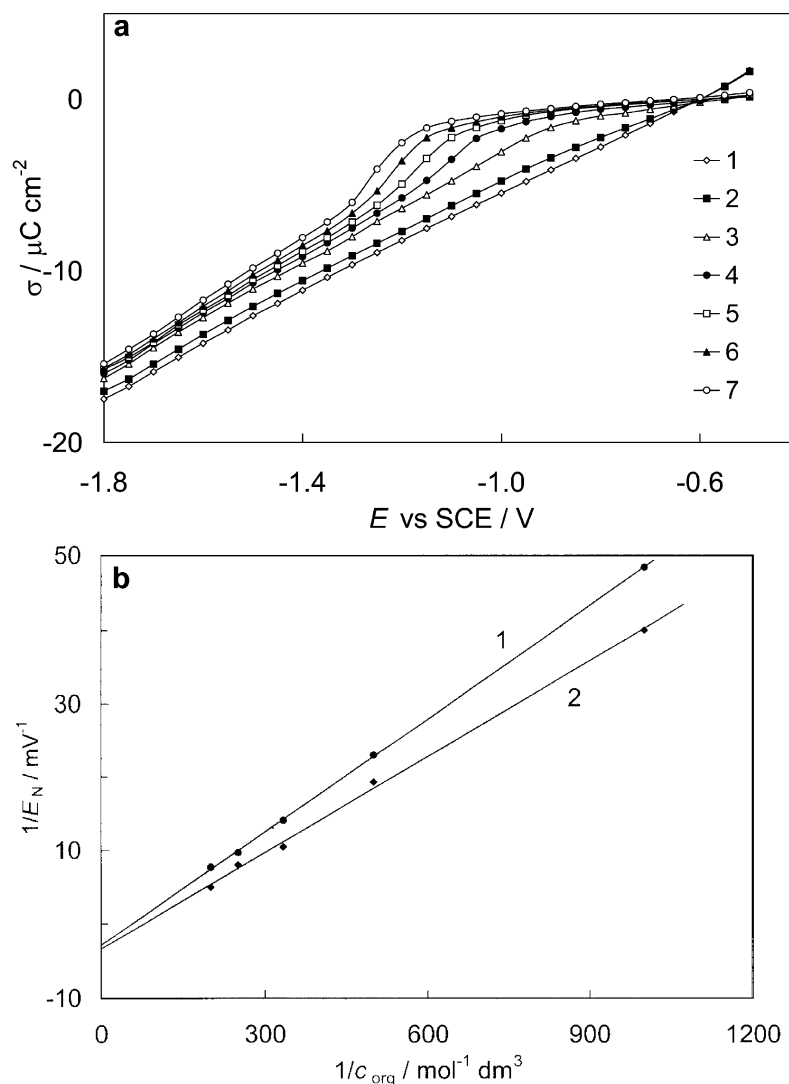
According to these data, there is weak, approximately linear, dependence of $\Delta E_{\min} = E_{\min}^{\text{org}} - E_{\sigma=0}$ on $1/c_{\text{org}}$, but this dependence is very small ($|\Delta E_{\min}| \leq 30$ mV) in comparison with the smaller aliphatic compounds adsorbed at Bi planes [23, 24, 25, 26] as well as with the data for adenosine [10]. Thus, the maximal adsorption of 1-HepOH from more concentrated solutions take place at only a very slightly negatively charged Bi surface, indicating that the limiting potential shift of zero charge potential, E_N , obtained according to the model of two parallel capacitors [34, 35]:

$$E_N = -[(E_{\max} - E_{\sigma=0})(C_0 - C_1)]/C_1 \quad (2a)$$

$$E_N = 4\pi\Gamma_{\max}(\mu_{\text{org}} - n\mu_{\text{H}_2\text{O}}/\epsilon) \quad (2b)$$

where Γ_{\max} is the limiting Gibbs excess and μ_{org} and $\mu_{\text{H}_2\text{O}}$ are the dipole moments of organic compound and water normal to the electrode surface respectively, and n is the number of H_2O molecules replaced by one 1-HepOH molecule, is very close to zero. Thus, the effective dipole moment for adsorbed 1-HepOH molecules

Fig. 5 **a** σ vs. E curves obtained from impedance ($\omega=0$) for Bi(111) in 0.05 M Na_2SO_4 (1) and with addition of 1-HepOH (M): 0.0005 (2); 0.0006 (3); 0.001 (4); 0.002 (5); 0.003 (6); 0.004 (7). **b** Dependence of $1/E_N$ on $1/c_{\text{org}}$ for Bi(011) (1) and Bi(111) (2)



($\bar{\mu} = \mu_{\text{org}} - n\mu_{\text{H}_2\text{O}}$) is characteristic for the practically planar orientation of 1-HepOH molecules at bismuth planes. Additionally, the value of the potential of maximal adsorption, E_{max} , has been obtained by the $[C_{\text{org}}(\omega=0) - C_0(\omega=0)] - E$ curves method [27, 30] and there is a good agreement of E_{max} values obtained by these two different methods. However, it is to be noted that the method mentioned above is not very exact or sensitive [27].

At $\sigma \leq -10 \mu\text{C cm}^{-2}$, the $\sigma - E$ curves with addition of 1-HepOH are practically parallel but not coincident with the $\sigma_0 - E$ curve for the base electrolyte (Fig. 5a). Thus the capacitance data can be used to determine 1-HepOH adsorption parameters only in the region of maximal adsorption. In the region of adsorption-desorption peaks the values of $C(\omega \rightarrow 0)$ obtained are non-equilibrium and cannot be used for obtaining $\sigma - E$ curves.

The values of the initial and final potentials for the potential step chronocoulometric experiments were chosen with the help of the $C - E$ and cyclic voltammetric $i - E$ curves. The initial potential E_i was varied from -0.40 to -1.70 V (SCE). The values of $E_{\text{min}}^{\text{org}}$, corresponding to the zero charge potential of system with the additions of 1-HepOH in 0.001 M Na_2SO_4 , have been used for the construction of $\sigma - E$ curves. The final potential E_f was equal to -1.60 V (SCE) for $c_{\text{org}} \leq 0.001$ M and -1.70 V (SCE) for $c_{\text{org}} > 0.001$ M. This value was chosen carefully in order to: (1) achieve the complete desorption of 1-HepOH and (2) keep the current of hydrogen evolution small enough so that the faradaic reaction would not interfere with the determination of the electrode charge density [8, 9, 22, 23, 24, 25, 33, 52, 53]. Five series of step experiments were made for 1-HepOH concentrations from 1×10^{-4} to 7×10^{-3} M. The $\sigma - E$ curves were calculated according to method described by Lipkowski et al. [54, 55, 56, 57]. The precision of the charge measurements was about 2–3%.

The comparison of the $\sigma - E$ data for the capacitance and potential step measurements (Fig. 5b) shows that the values of $\Delta\sigma$ obtained by chronocoulometry are somewhat higher than data obtained from impedance at $\sigma \leq -10 \mu\text{C cm}^{-2}$, i.e. for $E < E^{\text{peak}}$. The difference between the values of σ obtained by these different methods does not exceed $\pm 1.5 \mu\text{C cm}^{-2}$ in the region of $E > E^{\text{peak}}$, which is only slightly higher than the experimental error for obtaining the σ values. The deviation of $\sigma - E$ curves at $E \leq E^{\text{peak}}$, obtained from impedance, from the chronocoulometric $\sigma - E$ curves indicates that, in spite of the extrapolation of $C - E$ curves to $\omega = 0$, these curves are not exactly equilibrium [52, 53, 54, 55, 56, 57, 58, 59, 60]. Another explanation would be that slow cathodic processes are possible at $E < E^{\text{peak}}$ and the extrapolation of the $\Delta\sigma - t$ curves to $t \rightarrow \infty$ gives somewhat higher values of total charge density values $\Delta\sigma_{\Sigma}$, caused by the faradaic component of process $\Delta\sigma_{\text{far}}$, i.e. $\Delta\sigma_{\Sigma} = \Delta\sigma_{\text{edl}} + \Delta\sigma_{\text{far}}$, where $\Delta\sigma_{\text{edl}}$ is the charge density caused by the edl formation. Comparison of the charge-potential data for 1-PrOH, 1-BuOH, 1-PenOH, CyOH, 1-HexOH and 1-HepOH [7, 8, 10, 11, 51] shows that the difference

between σ values obtained by these methods increases in the sequence of adsorbates as $1\text{-PrOH} < 1\text{-BuOH} < 1\text{-PenOH} < \text{CyOH} < 1\text{-HexOH} < 1\text{-HepOH}$ as the adsorption activity of the organic compound at the electrode increases. It is to be noted that the chronocoulometric method is very sensitive to the value of the zero charge potential used as well as to the slow hydrogen evolution process [probable at $E < -1.5$ V (SCE)], and therefore the difference of σ values obtained by impedance and chronocoulometry methods may be caused by these two factors. Therefore, the quantitative data presented in this work are mainly obtained from the impedance data at $\omega = 0$ obtained from the $\sigma - E$ curves and calculated using $E_{\sigma=0}^{\text{org}}$ values.

The charge density σ_{max} , at which the maximum adsorption takes place, slightly depends on the plane, and the absolute value of σ_{max} rises in the order $(01\bar{1}) \leq (001) < (111)$. The linear segments were observed on the $\sigma - E$ curves close to E_{max} . The difference between these values and the value of $E_{\sigma=0}$ for the pure base electrolyte solution is equal to the change in the surface potential due to the displacement of a monolayer of water molecules by a monolayer of 1-HepOH (E_N). The established values of E_N are very close to zero for all planes studied ($E_N \leq 10$ mV). The values at E_N decrease in the order 1-PrOH ($E_N = 0.33$ V), 1-BuOH ($E_N = 0.24$ V), 1-PenOH ($E_N = 0.21$ V) and 1-HexOH ($E_N = 0.20$ V) if the adsorption of the aliphatic alcohols takes place at an Hg electrode from 0.1 M NaF aqueous solution [25, 26, 27, 33] and for a polycrystalline Bi electrode [15, 17] in the order 1-PrOH ($E_N = 0.30$ V), 1-BuOH ($E_N = 0.27$ V), 1-PenOH ($E_N = 0.23$ V), 1-HexOH ($E_N = 0.20$ V) and 1-HepOH ($E_N = 0.18$ V). The lower values of E_N for the Bi planes indicate that the adsorbed 1-HepOH molecules have a practically flat orientation on the Bi planes|1-HepOH interface in comparison with that for Hg.

Specific surface work and film pressure curves

The $\sigma - E$ curves (at $\omega = 0$) were back-integrated to obtain a specific surface work decrease ($\gamma - \gamma_0$) as a function of the electrode potential and adsorbate concentration [7, 9, 10, 22, 23, 24, 25, 51]. A good accordance between $(\gamma - \gamma_0) - E$ curves, obtained from capacitance-potential and potential step measurements [$\Delta(\gamma - \gamma_0) = \pm 0.50 \mu\text{J cm}^{-2}$], can be seen between -8 and $3 \mu\text{J cm}^{-2}$, where the thermodynamic analysis takes place.

The pressure of the film of adsorbate π can be determined as:

$$\pi(E) = \gamma_{c=0} - \gamma_c = \int_{E_0}^E \sigma_c dE - \int_{E_0}^E \sigma_{c=0} dE \quad (3)$$

where the subscripts c and $c=0$ indicate the presence or absence of the adsorbate in the bulk of the electrolyte, respectively. The calculated $\pi - E$ curves are plotted in

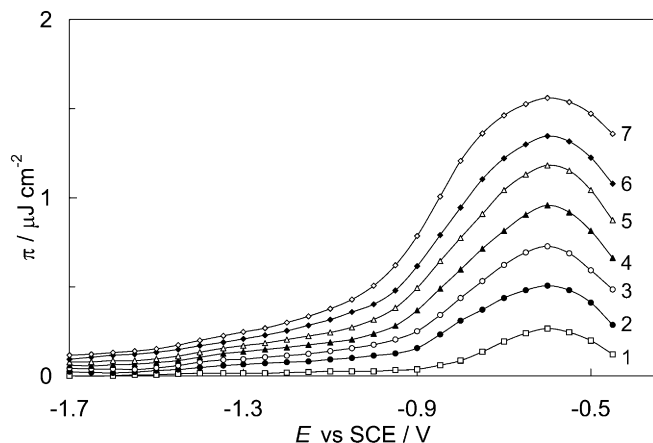


Fig. 6 Surface pressure vs. potential (π - E) curves for Bi(001) ($\omega=0$) in 0.05 M Na_2SO_4 aqueous solution with addition of 1-HepOH (M): 0.00045 (1); 0.0007 (2); 0.00085 (3); 0.001 (4); 0.002 (5); 0.0025 (6); 0.003 (7)

Fig. 6. For more concentrated solutions of 1-HepOH ($c \geq 0.0002$ M) the curve displays a maximum, the potential of which is practically independent of c_{org} , and this value is in agreement with the value of E_{max} from C - E curves. The comparison of the π - E curves, obtained from capacitance-potential ($\omega=0$) and potential step measurements, shows that the departure of the Bi|1-HepOH system from equilibrium is small in the region of maximal adsorption potentials. The film pressure of the adsorbate at $c_{\text{org}} = \text{const.}$ increases in the sequence of compounds as 1-PrOH < 1-BuOH < 1-PenOH < 1-HepOH < 1-HexOH (Fig. 7). Accordingly, the adsorption activity of the compounds increases in the presented sequence of adsorbates.

The adsorption activity of bismuth electrodes increases in the sequence of planes as (111) < (001) < (01 $\bar{1}$) as the surface density of the atoms increases [except for Bi(111)]. This deviation is evidently determined by the competitive adsorption of water and the organic substance, as well as by the crystallographic and electronic structure of the electrodes. Just as in the case of other aliphatic alcohols [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 51], the basal plane (111), where the surface atoms are chemically saturated (electron configuration sp^3d^2) [61], has the lowest adsorption activity. The most active one is the singular face Bi(01 $\bar{1}$), where unsaturated covalent bonds are distributed uniformly over the whole surface.

Gibbs excess vs. potential and Gibbs excess vs. $\log c_{\text{org}}$ curves

Film pressure data were used to calculate the relative Gibbs surface excess values. First the film pressure was plotted against $\ln c_{\text{org}}$ at $E = \text{const.}$ (Fig. 8). The curves display a linear section at higher 1-HepOH concentrations and its slope gives the limiting value of Γ_{max} :

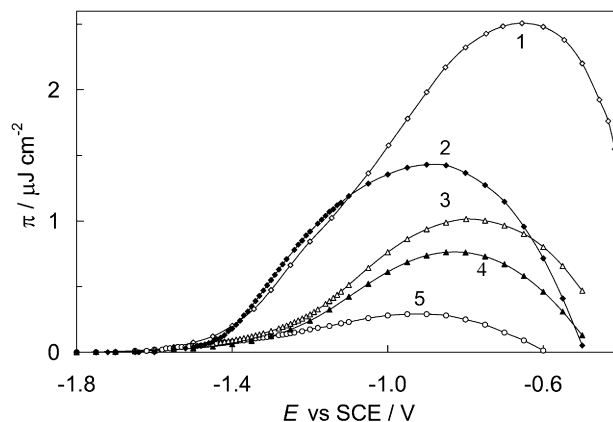
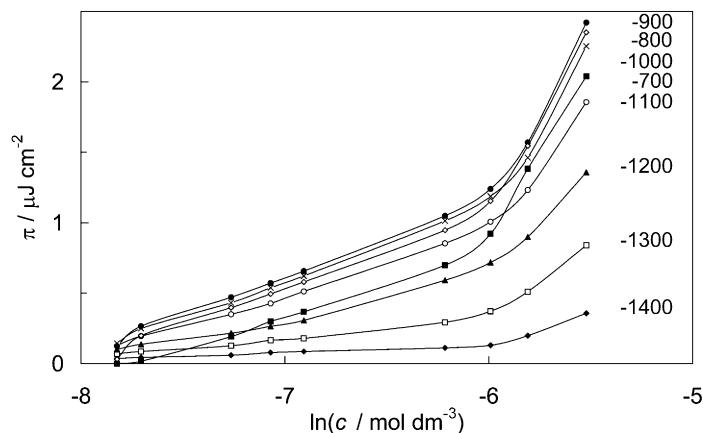


Fig. 7 π vs. E curves for Bi(001) ($\omega=0$) in 0.05 M Na_2SO_4 with addition of various alcohols: 0.006 M 1-HepOH (1); 0.04 M 1-HexOH (2); 0.02 M 1-PenOH (3); 0.01 M 1-BuOH (4); 0.2 M 1-PrOH (5)

$$\Gamma = \frac{1}{RT} \left(\frac{\partial \pi}{\partial \ln c} \right)_{E,T,p} \quad (4)$$

As the mole fraction of 1-HepOH never exceeded 0.1%, at a first approximation it was assumed that the activity of 1-HepOH depends linearly on its concentration according to Henry's law [7, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 56, 57, 58]. The values of Γ_{max} obtained for 1-HepOH are presented in Table 1 and comparison of these data with previous data [3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 51] shows that Γ_{max} only very slightly decreases in the sequence of adsorbates 1-PrOH > 1-BuOH \geq 1-PenOH \geq 1-HexOH \geq 1-HepOH as the molar volume of the organic compounds increases. Thus for longer linear alcohols this decrease is very small. Calculated according to the values of Γ_{max} , the values of the molecular surface area, S_{max} (Table 1), corresponding to the area of one adsorbed molecule on the electrode surface at the maximum adsorption potential E_{max} , decrease in the order of the Bi planes as (01 $\bar{1}$) > (111) \geq (001). The value of S_{max} should be the same for all linear aliphatic compounds (Fig. 9) and would be equal to $S_{\text{max}}^{\text{theor}} \approx 0.21 \text{ nm}^2$ [27, 28], corresponding to $\Gamma_{\text{max}}^{\text{theor}} = 7.9 \times 10^{-10} \text{ mol cm}^{-2}$ if the adsorbed linear aliphatic alcohol molecules were oriented perpendicularly at the Bi|electrolyte interface. The same conclusion would be valid if the orientation of adsorbed molecules is independent of the crystallographic structure of the electrode surface. The noticeable higher values of the projected area S_{max} for 1-HepOH, 1-HexOH, 1-PenOH and 1-BuOH indicates that the vertical orientation is not valid for the Bi|aliphatic alcohol interface. Therefore the theoretical $\Gamma_{\text{max}}^{\text{theor}}$ values have been calculated according to the equation $\Gamma_{\text{max}}^{\text{theor}} = V_m^{-2/3} N_A^{-1/3}$ [62], where the molar volume of adsorbate V_m has been used. According to the data in Fig. 9, for less active Bi(111) and Bi(001) planes the longer linear aliphatic alcohols have $\Gamma_{\text{max}}^{\text{exp}}$ values in good agreement with $\Gamma_{\text{max}}^{\text{theor}}$. For Bi(01 $\bar{1}$) the $\Gamma_{\text{max}}^{\text{exp}}$ values are lower than $\Gamma_{\text{max}}^{\text{theor}}$ and the practically flat

Fig. 8 π vs. $\ln c$ curves for Bi(001) ($\omega = 0$) at different electrode potentials (mV vs. SCE), as noted on the figure



orientation seems to be probable for 1-HexOH and 1-HepOH on Bi(01 $\bar{1}$) planes [23, 33, 42]. This conclusion is in good accordance with the very weak exchange of E_N and $\bar{\mu}_{\text{eff}}$ values for 1-HepOH, 1-HexOH and 1-PenOH compared with 1-PrOH and 1-BuOH. The decrease of Γ_{max} values is in good agreement with the noticeable decrease of the attractive interaction constant α in the sequence of planes Bi(001) \geq Bi(111) $>$ Bi(01 $\bar{1}$). The same tendency is valid for Ag, Hg and Zn(0001) electrodes if the adsorption of aliphatic alcohols occurs [20, 21, 22, 27, 33, 39, 40].

As in the bent region of the π - $\ln c$ curves, the slope changes noticeably and the error of differentiation of π - $\ln c$ curves is large [23]; the related Gibbs excess values for the intermediate coverages were determined from the electrode charge densities using the well-known formula [24, 27]:

$$\Gamma = \frac{\sigma_{\Gamma} - \sigma_{\Gamma=0}}{\sigma_{\Gamma_{\text{max}}} - \sigma_{\Gamma=0}} \Gamma_{\text{max}} \quad (5)$$

The values of $\sigma_{\Gamma_{\text{max}}} - \sigma_{\Gamma=0}$ were obtained by extrapolation of the linear sections of the σ - E curves. The shapes of the Γ - E curves for different c_{org} and of the Γ - $\log c$

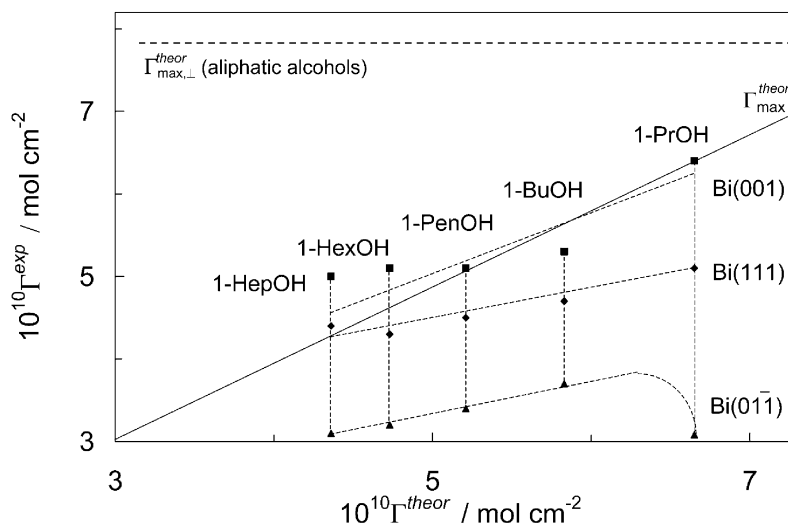
curves (Figs. 10 and 11) suggest that the relative maximum of the adsorption of 1-HepOH on all the planes investigated is reached at $-0.7 < E < -1.3$ V (SCE) and Γ_{max} depends on the crystallographic structure of the surface. The values of Γ_{max} increase in the order of electrodes as (01 $\bar{1}$) $<$ (111) $<$ (001) and these values are in good accordance with Γ_{max} values obtained from π - $\ln c$ curves. The slope of the Γ - E curves in the region of intermediate values of Γ ($c_{\text{org}} = \text{const.}$) increases in the order of planes as (01 $\bar{1}$) $<$ (111) $<$ (001) and in the order of adsorbates as 1-PrOH $<$ 1-BuOH $<$ 1-PenOH $<$ 1-HepOH $<$ 1-HexOH $<$ CyOH as the attraction between the adsorbed molecules rises. The value of Γ_{max} increases in the sequence of electrodes as Ag(100) $<$ Ag(111) $<$ Bi(01 $\bar{1}$) $<$ Bi(111) $<$ Bi(001) $<$ Hg [23, 33].

Adsorption isotherms

The surface coverage at $E = E_{\text{max}}$ was first estimated from Eq. 6 based on Frumkin's two parallel condensers model [22, 27, 33]:

$$\theta = (C_0 - C_{\theta}) / (C_0 - C_1) \quad (6)$$

Fig. 9 Dependence of $\Gamma_{\text{max}}^{\text{exp}}$ for various aliphatic alcohols on the value of $\Gamma_{\text{max}}^{\text{theor}}$ at Bi single-crystal electrodes



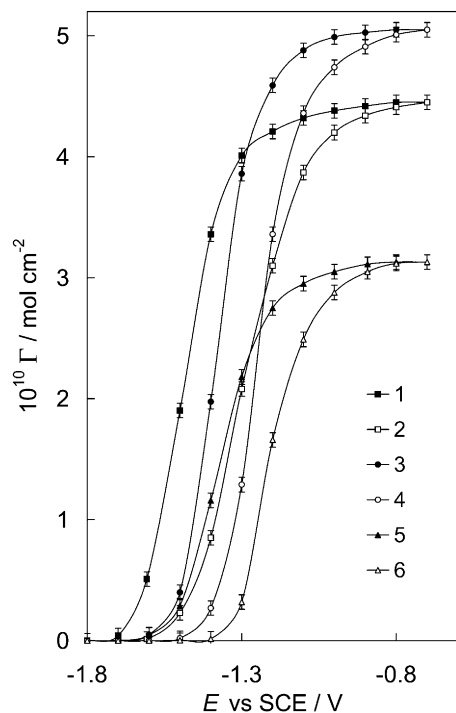


Fig. 10 Gibbs excess vs. potential (Γ - E) curves for Bi(001) (1, 2); Bi(111) (3, 4); and Bi(011) (5, 6) with different additions of 1-HepOH (M): 0.004 (1, 3, 5); 0.002 (2, 4, 6)

Thereafter, at a first approximation, the applicability of the Frumkin isotherm:

$$B_m c = \frac{\theta}{1 - \theta} \exp(-2\alpha_m \theta) \quad (7)$$

for the interpretation of 1-HepOH|Bi data was assumed. In Eq. 7, B_m and a_m are the adsorption equilibrium constant and the molecular interaction parameter at E_{\max} , respectively. The next step is the test of the Frumkin isotherm ($\log[\theta/(1-\theta)c]$ versus θ plot) to derive the adsorption parameters. Figure 12 shows that the plots have a good linearity in the region of $0.1 < \theta < 0.9$ for all the faces investigated. Thus, the slope gives the molecular interaction parameter ($-2a_m$) and the intercept provides the adsorption equilibrium constant $\log B_m$ at E_{\max} accordingly.

The adsorption isotherms at various $E = \text{const.}$ and at various $\sigma = \text{const.}$ were calculated by the methods described elsewhere [7, 8, 9, 10, 11, 12, 20, 21, 22, 23, 24, 25, 26, 27, 28, 63, 64, 65]. The adsorption isotherms at $\sigma = \text{const.}$ show larger deviations from the Frumkin isotherm behaviour than those at $E = \text{const.}$, where the deviations in the region $-0.6 < E < -1.2$ V (SCE) are small.

Gibbs adsorption energy vs. potential
and lateral interaction vs. potential curves

The energetics of 1-HepOH adsorption are characterized by the magnitude of the Gibbs energy of adsorption (Fig. 13). In the limit of zero coverage the adsorption of

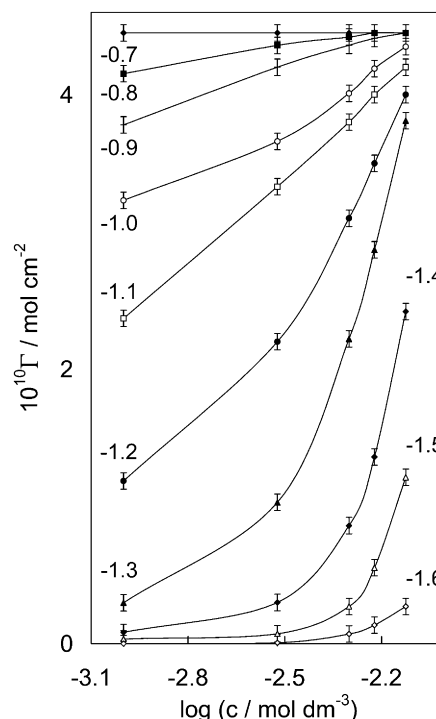


Fig. 11 Γ vs. $\log c$ curves for Bi(111) at different electrode potentials [in V (SCE)] as noted on the figure

1-HepOH must be described by Henry's law isotherm and the film pressure should then linearly depend on the concentration of 1-HepOH, as described by the following equation [8, 9, 10, 11, 12, 20, 21, 22, 23, 24, 25, 26, 27, 63, 64, 65]:

$$\pi = RT\Gamma_{\max} B_A c_A / 55.5 = RT\Gamma_{\max} B_A X_A \quad (8)$$

where X_A is the mole fraction of 1-HepOH in the solution, and the adsorption equilibrium coefficient B_A (Henry isotherm) is related to the Gibbs energy of adsorption through the equation:

$$\Delta G_A^\circ = -RT \ln B_A \quad (9)$$

As shown in [55, 56, 57, 63, 64, 65], the values of $-\Delta G_A^\circ$ obtained according to Eqs. 8 and 9 correspond to the similar standard state as the Gibbs adsorption energy of an organic compound, obtained according to the Frumkin isotherm, being the unit mole fraction of the organic species in the bulk of the solution and a monolayer coverage of the ideal non-interacting adsorbate at the electrode surface. According to the data of Fig. 13, the $-\Delta G_A^\circ$ vs. E curves have a nearly parabolic shape which is in good agreement with the Frumkin-Damaskin adsorption theory [27, 30] and can be explained by the quadratic dependence of the adsorption energy of the uncharged organic compound (i.e. the adsorption equilibrium constant value) on the applied electrode potential. It must be noted that the precision of $-\Delta G_A^\circ$ values obtained by this method is improved by avoiding the differentiation of $\pi - \ln X_A$ plots, as the values of Γ_{\max} , obtained from the linear part of the $\pi - \ln c$

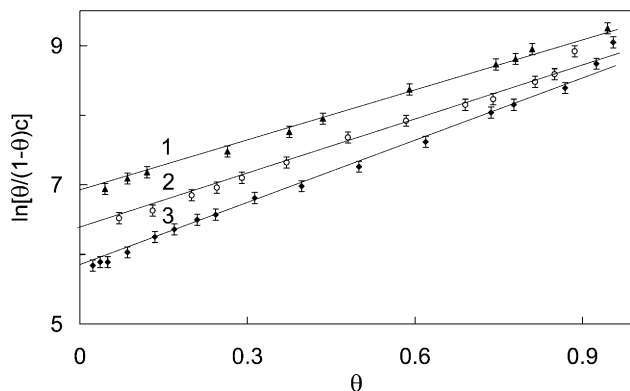


Fig. 12 Frumkin adsorption isotherm ($\omega=0$) for 1-HepOH adsorption on Bi single-crystal planes: Bi(011) (1); Bi(001) (2); Bi(111) (3)

plots, are quite precise [7, 8, 9, 10, 11, 12, 22, 23, 24, 25]. Thus, the precision of the film pressure data must be very high in order to obtain the precise values of $-\Delta G_A^\circ$. Therefore, in addition to the previously described method, the standard Gibbs energy of adsorption $-\Delta G_A^\circ$ at zero coverage as a function of the applied potential E was obtained by fitting the experimental isotherms at $E=\text{const.}$ to the Frumkin isotherm:

$$X_A \exp\left(\frac{-\Delta G_A^\circ}{RT}\right) = \frac{\theta}{1-\theta} \exp(-2\alpha\theta) \quad (10)$$

where α is the Frumkin interaction parameter. The values of $-\Delta G_A^\circ$ and α were obtained from the intercepts and slopes of the least-squares fittings to a straight line of $\ln[\theta/(1-\theta)c]$ versus θ plots at $E=\text{const.}$ in the range of θ from 0.1 to 0.9. A good fit to Eq. 10 was achieved with the parameter α depending nearly parabolically on the electrode potential (Fig. 14). This result shows that the value of the projected area of the organic compound at the electrode surfaces decreases approximately linearly as the surface coverage θ increases [27, 30]. The accordance of the Gibbs energies of the 1-HepOH adsorption, obtained from π -lnc plots and from the Frumkin isotherm, is good (maximum error does not exceed $\pm 1.5 \text{ kJ mol}^{-1}$), which indicates the absence of large systematic errors in the data established. The values of $-\Delta G_A^\circ$ obtained from π -lnc plots are always somewhat higher than those obtained from the Frumkin isotherm. This difference increases if the adsorption activity of the organic compound rises [8, 9], thus as its molecular weight and molar volume increase.

The adsorption data for 1-HepOH on the Bi single-crystal planes are collated in Table 1, and show that the adsorption activity of 1-HepOH increases in the sequence of planes as (111) < (001) < (011). The adsorption activity of 1-HepOH at Bi(001) is very close to that for the polycrystalline bismuth solid drop electrode [15], and the lower adsorption activity of Bi(111) is caused mainly, in addition to the more pronounced water adsorption, by a less active surface state of Bi(111), where the surface atoms are chemically saturated. The

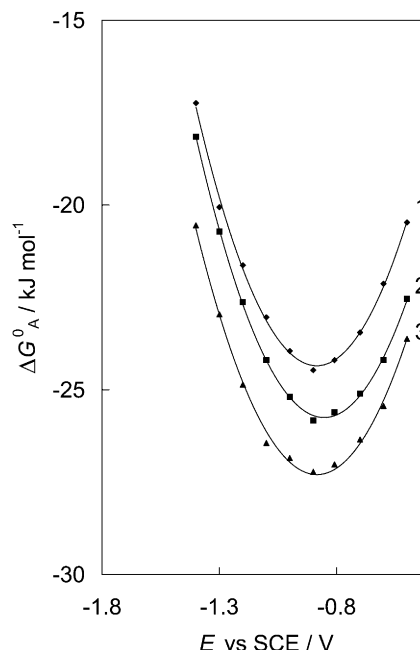


Fig. 13 Gibbs adsorption energy vs. potential curves for 1-HepOH ($\omega=0$) for Bi single-crystal planes: Bi(111) (1); Bi(001) (2); Bi(011) (3)

surface activity of adsorbates increases in the sequence 1-PrOH < 1-BuOH < CyOH < 1-PenOH < 1-HexOH < 1-HepOH as the adsorption at the air/solution interface increases [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12].

According to Figs. 14 and 15 the lateral interaction constants α are positive and their values decrease when the surface charge density decreases. Also according to Figs. 14 and 15, the attractive interaction at $E_{\sigma=0}$ and at E_{max} increases in the sequence of planes Bi(011) < Bi(001) < Bi(111). The same order of planes at E_{max} was found in the case of adsorption of 1-PrOH, 1-BuOH, 1-PenOH and 1-HexOH at Bi single-crystal electrodes [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 51]. In the case of adsorption of organic compounds at the metal surfaces from solution, the attractive interaction constant α can be expressed in terms of different particle-particle interactions at the interface [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 20, 22, 23, 24, 25, 26, 27, 28, 51, 66]:

$$2\alpha = (2Z_{W-A} - Z_{A-A} - Z_{W-W})/RT \quad (11)$$

where Z_{i-j} is the particle-particle interaction energy, W stands for H_2O and A for adsorbate. The positive values of α mean that $2Z_{W-A} > Z_{A-A} + Z_{W-W}$, i.e. the adsorbate-adsorbate and water-water interactions are much more attractive than the adsorbate-water interaction. According to the data (Fig. 15), the value of α has a maximum at $V_m=109$ and for longer aliphatic compounds α_0 is practically independent of the length, as well on the molar volume of adsorbate. The practically same value of α for 1-BuOH, 1-PenOH, 1-HexOH and 1-HepOH molecules indicates that the hydrocarbon tail of these compounds in the adsorption layer is not linear or

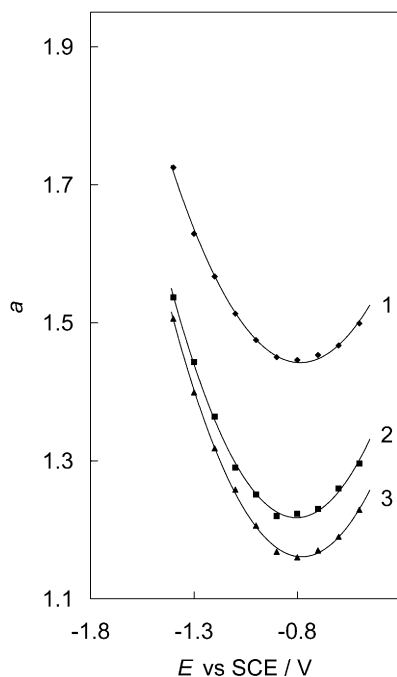


Fig. 14 Attraction interaction constant vs. potential curves for Bi(111) (1); Bi(001) (2); Bi(01 $\bar{1}$) (3)

these molecules will have the more tilted orientation. If we assume at a first approximation that the water-water and the organic compound-water interactions are independent of the aliphatic compound studied, then the attraction between the adsorbed aliphatic alcohol molecules rises in the order of adsorbates as 1-PrOH < 1-BuOH < 1-PenOH \leq 1-HepOH. The same order of adsorbates is valid in the case of the adsorption of aliphatic alcohols at Hg, Zn(0001), Zn(11 $\bar{2}$ 0), Zn(10 $\bar{1}$ 0), Ag(111), Ag(110) and Ag(100) electrodes [22, 23, 24, 25, 26, 27, 33, 39, 40]. The value of α for 1-HepOH adsorption increases in the order of electrodes as Bi(01 $\bar{1}$) < Bi(001) < Bi(111) < Hg [22, 23, 24, 27, 29, 46, 51].

Conclusions

The adsorption behaviour of 1-heptanol at singular Bi(111), Bi(001) and Bi(01 $\bar{1}$) electrodes has been studied by CV, impedance and chronocoulometry methods. The presented results indicate that the adsorption parameters of 1-HepOH depend on the crystallographic structure of the Bi planes. The adsorption parameters derived from the capacitance data, extrapolated to $2\pi f = \omega = 0$, at surface charge densities $-10 < \sigma < 4 \mu\text{C cm}^{-2}$ are in reasonable accordance with the data from the chronocoulometric measurements. The difference between impedance and chronocoulometric data diminishes when the adsorption activity of the compound decreases and, accordingly, the impedance data for higher aliphatic alcohols (at $\omega = 0$) are to some degree

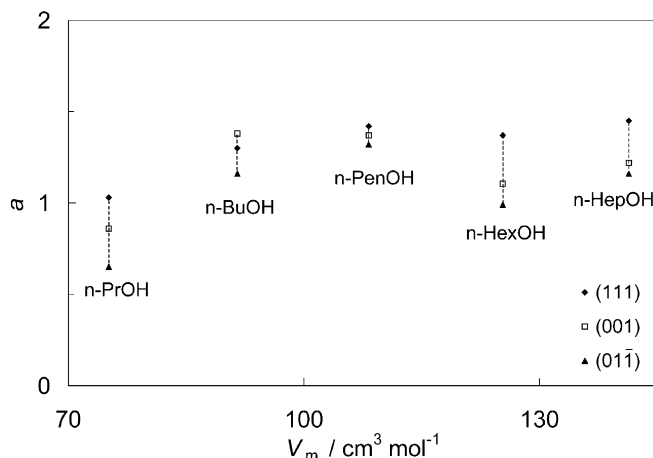


Fig. 15 Dependences of the molecular interaction parameter α on the molar volume V_m for various aliphatic alcohols at Bi single-crystal electrodes, as noted on the figure

non-equilibril in spite of extrapolation to $\omega \rightarrow 0$, but the data obtained from chronocoulometry are very sensitive to the value of zero charge potential used (especially E_N values), as well as to slow hydrogen evolution at negative polarizations [$E \leq -1.5$ V (SCE)]. Therefore the application of both methods seems to be very useful.

The comparison of the Gibbs energies of adsorption for various organic compounds shows that the adsorption activity of organic compounds at the Bi|solution interface increases in the order 1-PrOH < 1-BuOH < CyOH \leq 1-PenOH < 1-HexOH < 1-HepOH as the adsorption of organic compound at the air|solution interface rises. The difference between the adsorption activities of various Bi planes increases in the sequence of adsorbates as 1-PrOH < 1-BuOH < CyOH \leq 1-PenOH < 1-HexOH < 1-HepOH and thus the adsorption activity of an organic compound at the air|solution interface, as well as at the Bi|solution interface, rises. It was found that with the increase of the molar volume of adsorbate the changes in the adsorbed layer structure, caused by the adsorption of one molecule, rises in comparison with the adsorption of smaller surfactants.

The adsorption activity of 1-HepOH at Bi(001) is very close to that for the polycrystalline bismuth solid drop electrode [15], and the lower adsorption activity of Bi(111) is caused mainly, in addition to the more pronounced water adsorption, by a less active surface state of Bi(111), where the surface atoms are chemically saturated. The most active one is the singular Bi(01 $\bar{1}$) plane, where unsaturated covalent bonds are distributed uniformly over the whole surface.

The positive values of the lateral interaction constant α for 1-HepOH indicate that the surfactant-surfactant and water-water interactions are much more attractive than the surfactant-water interaction. The value of α increases in the order of adsorbates as 1-PrOH < 1-BuOH \approx 1-HexOH \approx 1-PenOH \approx 1-HepOH < CyOH as the molar volume of the adsorbate molecule increases, except for 1-PenOH, 1-HepOH and 1-HexOH. This result

probably indicates that the hydrocarbon tail of these compounds in the adsorption layer is not linear, as well as that these molecules have a tilted orientation.

The limiting Gibbs adsorption Γ_{\max} increases in the order of electrodes as $\text{Bi}(01\bar{1}) < \text{Bi}(111) < \text{Bi}(001)$ as the superficial density of planes decreases. The projected area S_{\max} decreases and Γ_{\max} increases in the order $1\text{-HepOH} \approx 1\text{-HexOH} \approx 1\text{-PenOH} \approx 1\text{-BuOH} \leq \text{CyOH} < 1\text{-PrOH}$. The decrease of Γ_{\max} and the increase of S_{\max} as the number of carbon atoms in the aliphatic alcohol molecule increases can be explained by an increasingly tilted orientation of the longer aliphatic alcohol molecules compared with 1-PrOH at the single-crystal $\text{Bi}(001)$ and $\text{Bi}(111)$ planes. Very low values of Γ_{\max} for 1-HepOH, 1-HexOH and 1-PenOH at the $\text{Bi}(01\bar{1})$ plane will indicate that these molecules probably have a practically flat orientation on the most active Bi plane.

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