A COMPARATIVE STUDY OF ADSORPTION OF ALIPHATIC AMINES AT A GOLD ELECTRODE

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Adsorption of aliphatic amines (C_1–C_4) at the gold electrode was studied by tensammetry. It has been established that the experimental dependence between the gold surface coverage (Θ) and the bulk amine concentration (c_A) fits satisfactorily both by the Frumkin and Flory–Huggins isotherms. The standard Gibbs energy of adsorption, ΔG°_{ad} at E_{max} for $\Theta < 0.8$ has been found to increase in the order methylamine < ethylamine < propylamine < butylamine. This is rationalised in terms of surface–adsorbate, adsorbate–adsorbate and adsorbate–solvent interactions.

Keywords: Amines; Adsorption; Gold electrode; Electrochemistry; Tensammetry; Thermodynamics.

The adsorption phenomena at the electrode/solution interface play an important role in the mechanisms of numerous reactions in electrosynthesis and electrocatalysis. Thus, comprehensive recognition of the adsorption properties of electrode materials towards substrates and reaction intermediates is required for modelling electrochemical systems and their practical applications.

The organic compounds selected for our study are aliphatic amines, widely used as starting or intermediate agents in the production of various chemical compounds such as polymers, corrosion inhibitors, pesticides as well as medicines. In spite of the unquestionable significance of aliphatic amines in industrial, clinical and environmental applications[1], their electrochemical behaviour has been scarcely examined. Studies at the gold electrode have been limited to voltammetric response of ethylamine[2–4] upon anodic oxidation in aqueous alkaline media. Similar data have been reported for platinum[5–10], silver[11–14] and mercury[15,16] electrodes. A few reports discuss the adsorption of aliphatic amines at a mercury electrode from aqueous solutions[17–20]. Up to now studies at gold surfaces were performed only for *n*-octylamine, *n*-dodecylamine, *n*-hexadecylamine and *n*-octadecylamine, in contact with a methanolic solution of $LiClO_4$ (ref.[21]).

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In this paper the adsorption behaviour of aliphatic amines ranging from methylamine to butylamine at the polycrystalline gold electrode/aqueous $NaClO_4$ solution has been characterised using tensammetry.

EXPERIMENTAL

The supporting electrolyte solution was prepared from doubly-recrystallised $NaClO_4$ (analytical grade, Fluka) and water purified in a Millipore Milli-Q system. Amines were of Aldrich analytical grade quality. Experiments were performed at 295 K with solutions deaerated with high-purity argon.

All measurements were conducted in a thermostated three-compartment cell using a polycrystalline gold bead (99.999%) of 0.3 cm^2 geometric area as a working electrode and a gold sheet as a counter electrode. A hydrogen electrode (RHE) in the supporting electrolyte solution as proposed by Will[22,23] was used as a reference electrode. For comparison with published data, all the potentials are quoted versus the saturated calomel electrode (SCE).

The C–E relationships were determined with the ac sinusoidal signal of 5 mV at 15 Hz superimposed on a slow linear electrode potential scan, $dE/dt = 5 \times 10^{-3}$ V s^{-1}. A slower scan rate did not affect the tensammetric curves. Additional measurements at various ac frequencies in the range from 5 to 40 s^{-1} did not show any frequency dispersion observed in the potential range $E = -1.1$ to 0.1 V vs SCE. Therefore, the capacity data at these potentials can be considered at equilibrium. The apparatus used in the voltammetric and tensammetric measurements was described elsewhere[24].

Prior to each series of measurements with amines, the working electrode was electrochemically activated by cycling ($dE/dt = 1 \times 10^{-1}$ V s^{-1}) in the potential range $E = -1.1$ to 0.75 V vs SCE in the supporting electrolyte solution (2×10^{-2} M $NaClO_4$), where no Faradic reactions occur at the gold surface. This procedure prevents structural changes of the gold surface. Furthermore, the roughness factor remains constant. When reproducible values of the differential capacitance of the double layer (C) were achieved, a roughness factor of 1.1 was calculated, assuming the differential double layer capacitance of a smooth gold electrode 22 μF cm^{-2} at E between –0.95 and –0.75 V vs SCE [25,26].

For each amine studied, a set of C–E curves was recorded, varying the amount of the surfactant in the bulk. The amine concentration (c_A) was increased from a minimum value, at which the C–E curve was almost comparable to that in the supporting electrolyte solution, up to the concentration at which further addition of the solute did not effect any change in the double layer capacitance.

RESULTS AND DISCUSSION

A representative set of C–E curves illustrating changes in the differential capacitance of the double layer as a function of the polycrystalline gold electrode potential, obtained in the supporting electrolyte solution (2×10^{-2} M $NaClO_4$) with various ethylamine and propylamine concentrations (c_A) are presented in Figs 1 and 2, respectively. The shape of the C–E curves for methylamine and butylamine is similar. Due to a low $NaClO_4$ concentration, any specific adsorption of ClO_4^- ions is avoided[25]. Thus, the position

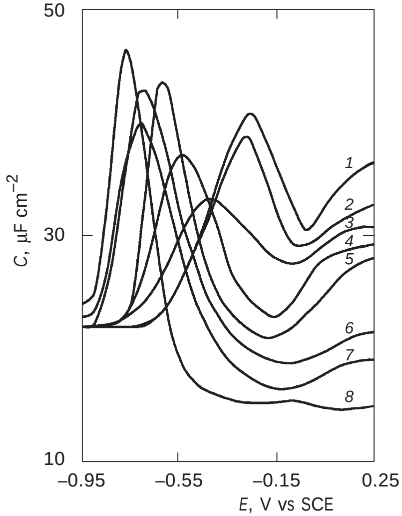

FIG. 1

Differential capacitance–potential (C–E) curves recorded at the gold electrode in 2×10^{-2} M $NaClO_4$ (curve *1*) and with increasing ethylamine concentration (mol dm^{-3}): 1.63×10^{-6} (*2*), 7.30×10^{-5} (*3*), 2.15×10^{-4} (*4*), 3.17×10^{-3} (*5*), 4.90×10^{-3} (*6*), 1.21×10^{-2} (*7*), 9.50×10^{-2} (*8*); dE/dt = 5×10^{-3} V s^{-1}

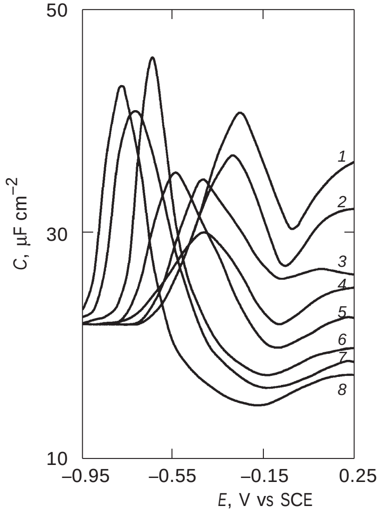

FIG. 2

Differential capacitance–potential (C–E) curves recorded at the gold electrode in 2×10^{-2} M $NaClO_4$ (curve *1*) and with increasing propylamine concentration (mol dm^{-3}): 8.85×10^{-6} (*2*), 2.87×10^{-5} (*3*), 6.10×10^{-5} (*4*), 1.06×10^{-4} (*5*), 7.60×10^{-3} (*6*), 1.66×10^{-2} (*7*), 9.50×10^{-2} (*8*); dE/dt = 5×10^{-3} V s^{-1}

of the pronounced capacitance minimum observed on the C–E curve for the gold electrode in the base solution at –0.04 V vs SCE can be assumed as the potential of zero charge (E_{pzc}). Note, that the evaluated E_{pzc} value is in a good agreement with those reported elsewhere for polycrystalline Au electrode[24,25,27], and for monocrystalline Au(110) electrode[28,29]. As shown in Figs 1 and 2, with increasing concentration of amines in the bulk solution, the differential capacitance significantly decreases, at first in a close proximity of E_{pzc} and then in an extensively broader potential range. This observation gives a clear evidence of the substitution of water at the gold surface with amine molecules. A progressive shift of the capacitance minimum towards lower electrode potentials implies the orientation of the dipolar amine molecules with the positive end of the dipole pointing towards the electrode surface.

Relatively strong adsorption of aliphatic (C_1–C_4) amines at gold is manifested by the fact that the C–E curves for the highest solute concentration at $E < -0.94$ V vs SCE do not coincide with the corresponding tensammeric curve of the supporting electrolyte solution electrode. This implies that some adsorbate molecules still remain at the electrode surface at potentials far lower than E_{pzc}.

Similarly as for alcohols and some other organic compounds[30–37], an increase in the amine concentration is accompanied by irregular changes in the capacitance maximum of the adsorption–desorption peaks appearing on the tensammetric C–E curves at $E << E_{pzc}$, i.e. at the negatively charged electrode surface. Therefore, the back integration procedure of the C–E curves cannot be used for the compounds under investigation in order to obtain information about the adsorbate surface concentration (Γ). Consequently, evaluation of the surface coverage $\Theta = \Gamma/\Gamma_{max}$ is possible only at the electrode potentials in the proximity of E_{pzc} (ref.[38]). The Θ values at certain concentration of each amine (c_A) were calculated by using the simplified Frumkin equation[18]

$$\Theta = (C_{\Theta=0} - C_{\Theta})/(C_{\Theta=0} - C_{\Theta=1}) \tag{1}$$

where $C_{\Theta=0}$, C_{Θ} and $C_{\Theta=1}$ denote the differential capacitances measured with the supporting electrolyte solution ($\Theta = 0$), at a certain coverage ($0 < \Theta < 1$) and at a limiting coverage ($\Theta = 1$) of the electrode surface, respectively.

The differential capacitance corresponding to the limiting coverage of the gold electrode with the adsorbed molecules ($C_{\Theta=1}$) was determined by extrapolation of the $1/C$ versus $1/c_A$ plot to $1/c_A = 0$, using the linear least squares method, for all amines studied at the potential of maximum adsorption E_{max} = –0.215 V vs SCE (Fig. 3). The E_{max} value was identified by commonly used analysis of the $\Delta C = C_{\Theta=0} - C_{\Theta=1}$ vs E dependence[39]. It should be mentioned that the obtained $C_{\Theta=1}$ values are close to these resulting directly from the experimental curves recorded for the highest concentration of each amine studied.

A characteristic feature is that the $C_{\Theta=1}$ value decreases gradually when passing from methylamine to butylamine (Table I). In view of the relation $C_{\Theta=1} = \varepsilon/4\pi x$ (refs[18,38]) and assuming that the electric permittivity (ε) does not change in the adsorbed layer, the above experimental finding suggests an increase in the thickness of the adsorbed layer (x) with increasing number of carbon atoms in the surfactant investigated (n_C). This supports a more or less perpendicular orientation of the carbon backbone of the adsorbed molecules at the gold/solution interface.

It should be argued that the E_{max} value of aliphatic amines on the investigated gold electrode is more negative than E_{pzc} measured in the supporting electrolyte solution. This fact once again indicates the preferential orientation of the adsorbed amine molecules with their carbon backbone directed towards the metal surface while the NH_2 group, having the lone electron pair localised on nitrogen atom and capable of interacting with gold, can be turned more or less towards the solution.

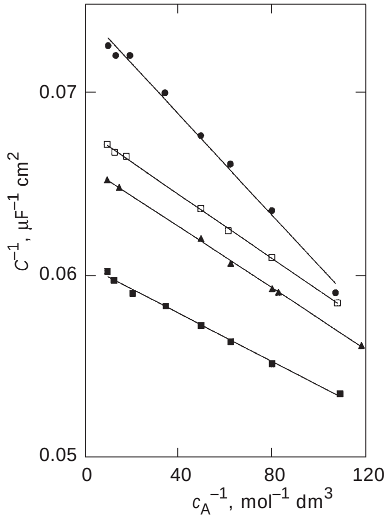

FIG. 3

The reciprocal of the experimental capacitance at E_{max} = –0.215 V vs SCE against the reciprocal of the concentration of: ■ methylamine, ▲ ethylamine, □ propylamine, ● butylamine adsorbed at the gold electrode in 2×10^{-2} M $NaClO_4$; dE/dt = 5×10^{-3} V s^{-1}

For each amine (C_1–C_4) studied, the relationship between the gold surface coverage (Θ) and the bulk amine concentration (c_A) at the potential E_{max} can be appreciably fitted to the Frumkin isotherm

$$[\Theta/(1 - \Theta)]\exp^{-2a\Theta} = \beta c_A \tag{2}$$

TABLE I
Adsorption parameters for aliphatic amines adsorbed at the gold electrode from 0.02 M $NaClO_4$ determined at E = –0.215 V vs SCE

Compound		$C_{\Theta=1}$ μF cm^{-2}	Frumkin isotherm			Flory-Huggins isotherm		
			lnβ	$-\Delta G^0_{ad}$ kJ mol^{-1}	a	lnβ	$-\Delta G^0_{ad}$ kJ mol^{-1}	n
Methylamine	$\Theta<0.8$	16.45 ±0.12	8.28 ±0.07	30.46 ±0.17	–0.33 ±0.01	7.93 ±0.09	29.60 ±0.22	1.39 ±0.15
	$\Theta>0.8$		6.40 ±0.05	25.81 ±0.12	0.25 ±0.01	6.77 ±0.16	26.72 ±0.40	0.95 ±0.06
Ethylamine	$\Theta<0.8$	15.10 ±0.10	9.38 ±0.05	33.19 ±0.12	–0.22 ±0.04	9.13 ±0.04	32.57 ±0.10	1.27 ±0.07
	$\Theta>0.8$		6.52 ±0.05	26.10 ±0.12	0.20 ±0.03	6.80 ±0.15	26.80 ±0.37	0.96 ±0.06
Propylamine	$\Theta<0.8$	14.66 ±0.09	10.32 ±0.04	35.52 ±0.04	–0.18 ±0.02	10.09 ±0.02	34.95 ±0.05	1.22 ±0.04
	$\Theta>0.8$		6.61 ±0.05	26.33 ±0.05	0.11 ±0.01	6.67 ±0.27	26.47 ±0.67	0.90 ±0.10
Butylamine	$\Theta<0.8$	13.40 ±0.13	11.28 ±0.03	37.90 ±0.07	–0.11 ±0.01	11.12 ±0.10	37.50 ±0.25	1.14 ±0.13
	$\Theta>0.8$		6.78 ±0.05	26.75 ±0.12	0.03 ±0.01	6.40 ±0.36	25.80 ±0.89	0.90 ±0.20

where β and *a* denote the adsorption equilibrium constant and the lateral interaction parameter, respectively. Figure 4 displays the plots [ln c_A – ln Θ/(1 – Θ)] versus Θ resulting from analysis of the *C*–*E* curves at E_{max}. Moreover, the interfacial behaviour of the compounds examined can be also represented by the Flory–Huggins isotherm

$$[\Theta/n(1 - \Theta)^n] = \beta c_A \qquad (3)$$

where *n* is the number of water molecules replaced by one adsorbate molecule at the electrode/solution interface. The respective plots of ln (Θ/c_A) versus ln (1 – Θ) at E_{max} are presented in Fig. 5.

Both types of isotherms for each amine studied reveal two regions of linear relationship in the above-mentioned plots for 0 < Θ < 0.8 and Θ > 0.8. The same observation was made for benzylamine adsorbed at Au electrode[33]. Consequently, two sets of adsorption parameters were collected. By using the linear least-squares method the values of ln β and ln (*n*β) were determined from the extrapolation of ln c_A – ln Θ/(1 – Θ) to Θ = 0 and ln (Θ/c_A) to ln (1 – Θ) = 0, respectively. The parameters *a* and *n* were evaluated from the slopes of the appropriate straight-line relationships for the isotherms tested. It should be emphasised that the values of β evaluated

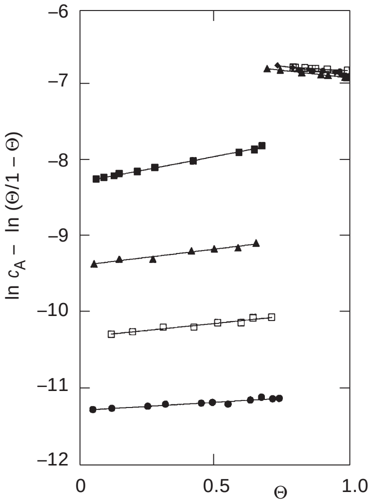

FIG. 4
Test of the Frumkin isotherm for: ■ methylamine, ▲ ethylamine, □ propylamine, ● butylamine adsorbed at E_{max} = –0.215 V vs SCE at the gold electrode in 2 × 10^{-2} M NaClO$_4$; d*E*/d*t* = 5 × 10^{-3} V s^{-1}

from both isotherms are close to each other. Taking as the reference state the unit mole fraction of amine in the bulk of the solution and a monolayer coverage of the surface with the ideal adsorbate, commonly used by various research groups[32], the standard Gibbs energy of adsorption (ΔG°_{ad}) was calculated from the relationship

$$\beta = [(1/55.5)\exp(-\Delta G^{\circ}_{ad}/RT)] \,. \tag{4}$$

The corresponding values of ln β, ΔG°_{ad}, a and n together with $C_{\Theta=1}$ values are summarised in Table I.

The effect of the molecular structure of the amines studied on their interfacial behaviour is clearly manifested by the adsorption parameters derived from the Frumkin and Flory–Huggins isotherms. The magnitude of the standard Gibbs energy indicates the physical nature of amines adsorption on the polycrystalline gold electrode. A characteristic feature is that the values of ΔG°_{ad} are more negative in the first region of the surface coverage ($\Theta < 0.8$) than those for higher surface coverages ($\Theta > 0.8$). The longer the carbon chain of the amine the greater these differences. As shown in Table I for $\Theta < 0.8$, the introduction of each subsequent CH_2 group into the carbon backbone of amine is accompanied by a progressive increase in the absolute value of ΔG°_{ad} by about 2.5 kJ mol^{-1}, while for $\Theta > 0.8$ this parameter re-

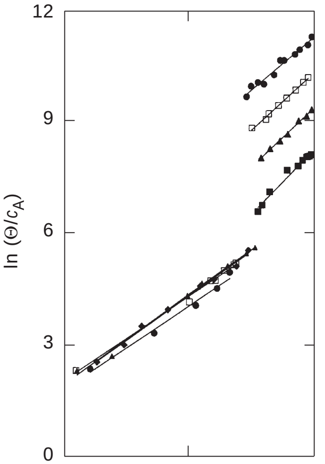

FIG. 5

Test of the Flory–Huggins isotherm for: ■ methylamine, ▲ ethylamine, □ propylamine, ● butylamine adsorbed at E_{max} = –0.215 V vs SCE at the gold electrode in 2×10^{-2} M $NaClO_4$; dE/dt = 5×10^{-3} V s^{-1}

mains almost constant regardless of the number of carbon atoms in the amine molecule.

Since the physisorption of organic molecules at the electrode/solution interface is in fact a replacement of the solvent molecules by those of the adsorbate, the ΔG°_{ad} value includes the contribution from the surface interactions between metal–solvent (G_{M-S}), metal–adsorbate (G_{M-A}), solvent–solvent (G_{S-S}) as well as adsorbate–adsorbate (G_{A-A}) and, further, the solvent–adsorbate (G_{S-A}) interaction both at the surface and in the bulk[40]. However, for a given metal/solution interface G_{M-S} and G_{S-S} are expected to be fairly independent of the nature of the adsorbed organic molecules. Hence, the variation of ΔG°_{ad} with increasing number of carbon atoms in the amine molecule should reflect mainly the changes in G_{M-A}, G_{A-A} and G_{S-A}. Taking into regard the values of the boiling temperature[41] an increase in the interaction energy between amine molecules when passing from methylamine to butylamine should be expected. Therefore, the ΔG°_{ad} value for butylamine more negative than that for methylamine can be explained in terms of stronger interactions between the adsorbate and the metal surface and/or reduced solvent–solute interaction.

It is worth noting that the ΔG°_{ad} values of amine adsorption on the gold electrode are much more negative (by about 30 kJ mol^{-1}) than those already determined for primary monohydric alcohols[32]. On the other hand, the value of increment $\Delta(\Delta G^{\circ}_{ad})$ per one carbon atom of amine is almost the same as that found for alcohols, thus confirming that the hydrophobic expulsion of the carbon backbone of organics from the liquid phase into the interface is similar for both groups of compounds. Consequently, the above described results indicate a higher energy of interactions between the NH_2 group of the surfactant and the metal surface when compared with those of the OH group. (A similar tendency has been also reported for the Hg electrode[18].) This conclusion is corroborated by the decrease in ΔG°_{ad} values at $\Theta > 0.8$, when with increasing packing there is a high probability of the NH_2 group moving away from the electrode surface.

Some further information on the interfacial behaviour of amine molecules can be obtained from the lateral interaction parameter (a) derived from the Frumkin isotherm. According to the relationship given by Trasatti at al.[42]

$$a = [G_{S-A} - 1/2(G_{A-A} + G_{S-S})]/RT \tag{5}$$

the negative value of the parameter a determined at $\Theta < 0.8$ for adsorption of aliphatic amines at E_{max} (see Table I), points to stronger water–amine

(S–A) interaction at the electrode/solution interface as compared with that among water–water (S–S) and amine–amine (A–A) interactions. The energy of the latter types of interactions must then increase on passing from methylamine to butylamine, as indicated by less negative values of *a*. This conclusion is in accordance with the finding that the absolute value of the standard Gibbs energy of adsorption, $|\Delta G^{\circ}_{\mathrm{ad}}|$, increases in the sequence methylamine < ethylamine < propylamine < butylamine. On the contrary for $\Theta > 0.8$, the lateral interaction parameter *a* takes small positive values, which means that the interactions between like particles become more attractive than those between unlike particles.

The above mentioned adsorption parameters (see Table I) point to changes in the arrangement of amine molecules with Θ. Most probably, the NH_2 group of the aliphatic amine molecules at $\Theta = 1$ is at the greatest distance from the gold surface while for $0 < \Theta < 0.8$ an approach of the NH_2 group towards the gold may be favoured. This would explain a slightly lower value of parameter *n* obtained from the Flory–Huggins isotherm for the region of $\Theta > 0.8$ as compared with that for $\Theta < 0.8$.

CONCLUSIONS

The aliphatic amines molecules adsorbing with their carbon backbone oriented towards the electrode surface assume a tilted arrangement for $\Theta < 0.8$, which favours an interaction of the NH_2 group with the gold surface. Specific interactions of this group with gold explain the higher $\Delta G^{\circ}_{\mathrm{ad}}$ values when compared with those for the respective monohydric alcohols. There is no doubt that the strength of these interactions becomes lower at $\Theta > 0.8$ when the functional group moves away from the electrode surface.

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