ADSORPTION OF THIOUREA ON MERCURY/DIMETHYL SULFOXIDE INTERFACE

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Adsorption of thiourea on mercury in the medium of 0·1M-$KClO_4$ in dimethyl sulfoxide was studied by measuring the dependence of the differential capacity on the potential. The parameters of the electric double layer were evaluated and the orientation of the solvent molecules on the electrode surface was discussed in terms of certain model concepts.

Thiourea (TU) serves as a preferred model compound in studying the compact part of the electric double layer[1-20] and, according to the literature[21,22], its adsorption enables to determine with the aid of certain model concepts the orientation of the solvent dipoles on the electrode surface. Adsorption of TU on mercury has been studied quantitatively not only in aqueous solutions[2,4] but also in methanol[5], N,N-dimethylformamide[6] (DMF), formamide[7] (F), N-methylformamide[8] (MF), and in 1,3-dioxolan-2-one (ethylene carbonate[21], EC).

The electrocapillary behaviour of TU differs from that of surface active substances which lower the capacity of the electric double layer in the region of the zero charge potential and give sharp capacitive peaks in the region of the desorption potential. In the presence of TU, in the potential region where it is adsorbed, an increase of the double layer capacity is observed. This can be attributed to a strong specific effect of the S atom in the TU molecule on the electrode surface. According to Frumkin[1], the adsorption of TU is similar to that of some anions, *e.g.* I^-. The form of the electrocapillary curves and the shift of the zero charge potential of mercury toward more negative values in the presence of TU in all solvents under study suggest that the TU dipoles are oriented with their negative end toward the mercury surface, namely – as shown in ref.[10] – perpendicularly to the surface. Capacitive curves of TU in such solvents as F and MF do not differ from those obtained with surface active anions in the same solvents. However, capacitive curves of TU measured in the medium of water, methanol, DMF, or EC show characteristic maxima. The reason for this difference is not known.

EXPERIMENTAL

Chemicals and Apparatus

Thiourea was purified by two-fold recrystallization from redistilled water and dried in vacuum. It was stored in an exsiccator under reduced pressure. Dimethyl sulfoxide (DMSO) was doubly distilled in vacuum and contained no more than 0·01 percent water. Its purity was checked by conductivity measurement (its specific conductivity was about $4 \cdot 10^{-8}\,\Omega^{-1}\,\text{cm}^{-1}$)[29]. Potassium perchlorate was triply recrystallized from redistilled water. Capacitive curves of the base electrolyte (0·1M-$KClO_4$ in DMSO) were measured and the differential capacity values were compared with literature data[29].

Differential capacity curves were measured at a frequency of 470 Hz on an R-568 type impedance bridge (USSR). The potential of the dropping mercury electrode was measured against normal calomel electrode.

RESULTS AND DISCUSSION

The differential capacity curves ($C-E$ curves) measured with a dropping mercury electrode in solutions of 0·1M-$KClO_4$ in DMSO containing $1 \cdot 10^{-3}$–0·3M-TU are shown in Fig. 1. Adsorption of TU causes an increase of the capacity in the potential region more positive than −0·9 V. At potentials more negative than −0·9 V the capacity curves in the presence and absence of TU are identical, an evidence for the absence of adsorption of TU. Therefore, the $C-E$ curves can be quantitatively evaluated by the method of reverse integration. A peculiar feature of the capacity curves in the presence of TU in the Hg/DMSO interface is a moderate adsorption maximum at higher concentrations (Fig. 1).

To calculate the surface excess of thiourea, Γ_{TU}, we used the surface pressure[3], $\Delta\xi$, and Gibbs' equation in the form

$$\Gamma_{TU} = (1/2{\cdot}3RT)\,(\partial\,\Delta\xi/\partial \log c_{TU})_q\,, \tag{1}$$

where R denotes gas constant, T absolute temperature, c_{TU} volume concentration of TU, and q surface charge of the electrode. The zero charge potential in the base electrolyte was obtained from ref.[23]. The dependence of $\Delta\xi$ on $\log c$ was differentiated both graphically and numerically by the QDFT 5 method[24].

We assumed that the adsorption of TU on mercury in the medium of DMSO is governed as in previous communications[8,10,18–20] by an isotherm with a virial coefficient:

$$\ln(\beta c) = \ln \Gamma + 2B\Gamma\,, \tag{2}$$

where β is an adorption equilibrium constant and B a parameter of mutual interaction of the adsorbed molecules. As in ref.[25], we calculated by the least squares method the values corresponding to minimum deviations from the theoretical isotherm of the surface pressure and further we calculated the values of Γ corresponding to this isotherm.

It is seen from Fig. 2 that all the given methods for calculating adsorption – graphical and numerical differentiation and Eq. (*2*) – agree satisfactorily (for $q = +3$ $\mu C/cm^2$). Adsorption isotherms of TU in DMSO for various surface charges of the electrode are shown in Fig. 3.

A linear dependence between $\log (\Gamma/c)_{TU}$ and Γ_{TU} (Fig. 4*a*) is an evidence that the adsorption of TU on the Hg/DMSO interface can be described by a virial isotherm. The coefficient of mutual repulsion B, determined from the data in Fig. 4*a*, diminishes from 22 to 5·3 nm^2 per molecule if the charge changes from -4 to $+3$ $\mu C/cm^2$. The dependence of the logarithm of the adsorption equilibrium constant β on the charge q is linear (Fig. 4*b*):

$$\log \beta = a + bq \,. \tag{3}$$

The parameter $a = -7{\cdot}5$ and $b = 0{\cdot}3$ $cm^2/\mu C$. The standard Gibbs adsorption energy ΔG^0_A calculated from β for $q = 0$ is $-92{\cdot}4$ kJ/mol.

The values of the standard Gibbs adsorption energy for TU in various solvents are given in Table I. Their mutual comparison shows that ΔG^0_A for thiourea on mercury is practically independent of the solvent character, apparently as a result of a strong specific effect of the S atom in the TU molecule on the electrode surface.

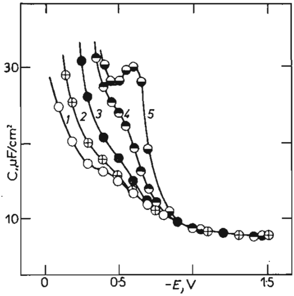

FIG. 1

Differential Capacity Curves for Dropping Mercury Electrode in 0·1M-$KClO_4$ in DMSO

Addition of TU: *1* 0; *2* 1 . 10^{-3}M; *3* 1 . 10^{-2}M; *4* 5 . 10^{-2}M; *5* 0·3M.

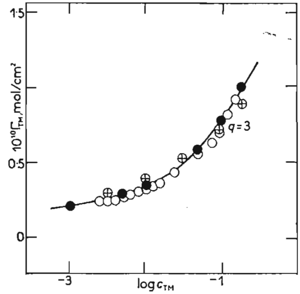

FIG. 2

Adsorption Isotherms for TU in Hg–DMSO Interface at Surface Charge $q = 3$ $\mu C/cm^2$

● Graphical, ○ numerical differentiation; ⊕ values calculated from the isotherm with virial coefficients. TM ≡ TU

A comparison of the adsorption of TU on mercury in the media of DMSO and MF reveals the influence of the adsorption parameters ΔG_A^0 and B (Table I).

TABLE I

Standard Gibbs Adsorption Energy ΔG_A^0 and Coefficient of Mutual Interaction of Adsorbed Molecules B for Various Solvents

Solvent	$-G_A^0$, kJ mol^{-1}	B, nm^2, mol^{-1}
Water	95·7	1·20
Methanol	—	1·50
Formamide	87·4	1·26
N-Methylformamide	91·5	3·80 for $q = -2$ μC/cm^2
		2·30 for $q = 6$ μC/cm^2
N,N-Dimethylformamide	90·3	4·10
1,3-Dioxolan-2-one	95·7	— —
Dimethyl sulfoxide	92·4	22·0 for $q = -4$ μC . cm^{-2}
		5·30 for $q = 3$ μC . cm^{-2}

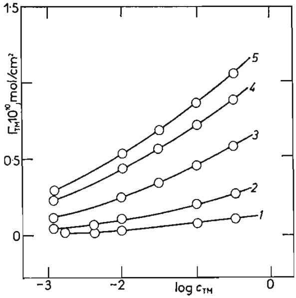

FIG. 3

Adsorption Isotherms for TU on Mercury in DMSO for Various Surface Charges (calculated from virial isotherm)

1 $q = -4$ μC/cm^2; *2* $q = -2$ μC/cm^2; *3* $q = 0$; *4* $q = 2$ μC/cm^2; *5* $q = 3$ μC/cm^2. TM ≡ TU

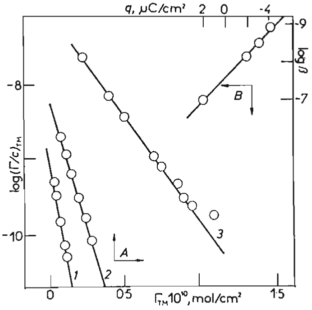

FIG. 4

Dependence of Functions

A $\log(\Gamma/c)_{TU}$ on Γ_{TU} for various surface charges

1 $q = -4$ μC/cm^2; *2* $q = -2$ μC/cm^2; *3* $q = 3$ μC/cm^2; *B* logarithm of adsorption equilibrium constant β on surface charge q. TM ≡ TU

The coefficient B for DMSO is twice as large as for MF, whereas the values of ΔG_A^0 are almost equal. Hence, in DMSO the adsorption of TU will be at an equal volume concentration weaker. This is in accord with the values for adsorption of TU on mercury in the medium of MF (ref.[8]).

Since in the medium of DMSO a specific adsorption of TU takes place, where the negative end of its dipole is directed toward the electrode surface, the obtained data can be used in the study of the structure of the compact part of the electric double layer.

Parsons[3] derived an equation for the change of the potential ψ^u in the compact layer:

$$\psi^u = (4\pi x_2/\varepsilon)\, q + (4\pi\mu_{ef}N_A/\varepsilon)\, \Gamma\,, \tag{4}$$

where x_2 denotes thickness of the compact part of the electric double layer, q surface charge of the electrode, ε permittivity of the compact layer, μ_{ef} effective dipole moment of the molecule in the adsorption layer, and N_A Avogadro's constant. The drop of the potential ψ^u can be determined from experimental data according to

$$\psi^u = E - E_{q=0} - \psi_0 = E_a - \psi_0\,. \tag{5}$$

The electrode potential E and the potential of zero charge $E_{q=0}$ are referred to the same reference electrode. The potential of the outer Helmholtz plane, ψ_0, in a uni-univalent electrolyte solution is calculated according to Graham's theory of the diffusion layer[26]:

$$\psi_0 = (2RT/F)\,\text{argsinh}\,(q/2A\sqrt{c})\,, \tag{6}$$

where $A = (RT\varepsilon_d/2\pi)^{1/2}$, ε_d denotes permittivity of the diffuse part of the double layer, c electrolyte concentration, and F Faraday's constant.

As follows from Eq. (*4*), the slope of the dependence of ψ^u on Γ is equal to $4\pi\mu_{ef}N_A/\varepsilon$ (Fig. 5). If we set the effective dipole moment equal to the dipole moment of an isolated TU molecule, the permittivity of the compact layer can be determined. Eq. (*4*) enables also to determine the integral capacity K_{02} of the compact layer:

$$K_{02} = \varepsilon/4\pi x_2\,. \tag{7}$$

If we set $\mu_{ef} = \mu_{TU} = 4{\cdot}89$ Debye units, then $K_{02} = 25\ \mu F/cm^2$.

The study of adsorption of TU is interesting since the TU molecule can serve as a test dipole whose insertion into the double layer enables to analyse its microstructure. This is important because the structure of the compact layer has been less extensively studied than the whole double layer; and the properties of the compact layer should reflect the specificity of the adsorbing particles and electrode material.

It was shown in the study of adsorption of TU on Hg in aqueous medium by Parsons that the thickness of the compact layer obtained from the electrostatic model is comparable with the dimensions of the water molecule. Garnish and Parsons[5] in their study of adsorption of TU on Hg in methanolic medium obtained (assuming that the effective dipole moment is equal to the dipole moment of an isolated TU molecule) the thickness of the compact layer from 0·45 to 0·25 nm when the surface charge changed from -5 to $+5\,\mu C/cm^2$. In the case of adsorption of TU on the Hg-DMF interface, Ganzhina and Damaskin[6] obtained on the basis of the Parsons' model improbably low values of the compact layer thickness x_2; acceptable values of x_2 could be obtained for $\mu_{ef} = 2\,\mu_{TM}$, which the authors attributed to a replacement of the DMF dipoles (oriented by their positive end toward the electrode surface) with the TU dipoles.

We attempted to apply the Parsons' model to our case. The calculated ψ^u potential as function of Γ_{TM} is shown in Fig. 5. The permittivity of the compact layer was determined for various electrode charges (Table II) with the assumption that $\mu_{ef} = \mu_{TM} = 4{\cdot}89$ Debye units. The value of ε can be calculated also according to

$$\varepsilon = (4\pi\mu_{ef}N_A/2{\cdot}3\boldsymbol{R}T)\,(\partial \log \beta/\partial q)_B \qquad (8)$$

as 6·5. We determined the value of x_2 which should correspond to the dimensions of the DMSO molecule in the adsorption layer. From the obtained parameters given in Table II, the thickness of the compact layer calculated by the Parsons' method lies close to 0·2 nm. The approximate diameter of the DMSO molecule calculated from the molecular mass and density is equal to 0·49 nm. From the known structure of the molecule[28], the length of the dipole, oriented with its positive end toward the electrode surface, is calculated as $x = 0{\cdot}56$ nm. Hence, the Parsons'

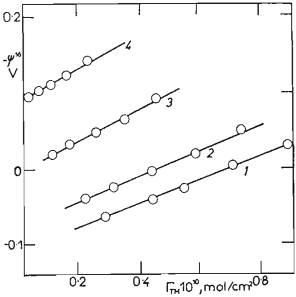

FIG. 5

Dependence of Potential in Compact Layer ψ^u on Adsorption of TU in Hg–DMSO Interface

1 $q = 3\,\mu C/cm^2$; *2* $q = 2\,\mu C/cm^2$; *3* $q = 0$; *4* $q = -2\,\mu C/cm^2$. TM ≡ TU model for $\mu_{ef} = \mu_{TU}$ is not adequate. To obtain a value of x_2 comparable with the dipole of the DMSO molecule, it is necessary to assume that its effective dipole moment in the adsorption layer is about twice as large as the dipole moment of an isolated TU molecule[6].

Naturally, the effective dipole moment of an adsorbed molecule differs from that of an isolated molecule because of a mutual interaction with the electric field of the electrode and with neighbouring solvent dipoles. To evaluate this effect, the Fawcett's model[21] is more suitable, involving polarization of adsorbed TU molecules under the influence of the electric field X formed by adsorbed solvent dipoles. The dipole moment is then given as

$$\mu = \mu_{TU} + \alpha X \,, \tag{9}$$

where α denotes polarizability of the molecules. The intensity of the electric field X is, in accord with Fawcett[21], determined according to the Levin–Bell's model[22]. These authors analysed the adsorption of TU in the Hg–EC interface and showed that (*a*) the EC dipoles are in the region of TU adsorption oriented with their positive end toward the electrode surface; (*b*) the use of the dipole moment value for TU according to (*9*) enables to determine the value of x_2 comparable with the dimensions of the EC molecule with an error of 15–20 percent.

To determine the effective value of the dipole moment changed by the electric field, we used Eq. (*9*) and the statistic model after Levin and Bell[22]. Its principle consists in the assumption that the compact layer is formed by a monolayer of solvent dipoles, which can be adsorbed in two different positions with respect to the electrode surface: $N\uparrow$ and $N\downarrow$ denote, respectively, the numbers of solvent molecules oriented with their negative or positive ends toward the electrode surface. The intensity of the electric field X is then given as

$$X = 4\pi\varrho q + n_{ef}\varrho\mu_s(\lambda - \delta)/x^3 \,, \tag{10}$$

TABLE II

Permittivity ε and Thickness of Compact Layer x_2 According to Parsons' Model and to Fawcett–Levine–Bell's Model (primed quantities)

q μC/cm²	ε Eq. (*4*)	x_2 nm	ε Eq. (*8*)	x_2 nm	ε'	x_2' nm
−2	5·0	0·18			9·7	0·35
0	5·5	0·19	6·5	0·22	12·0	0·45
3	7·0	0·25			15·0	0·53

where $\varrho = x^3/(1 + \alpha n_{cf})$, n_{cf} denotes effective coordination number of solvent molecules in the adsorption layer ($n_{cf} = 15{\cdot}2$) (ref.[21]), x length of the solvent molecule, μ_s its dipole moment, $\delta = \mathrm{tg}^2\,(\gamma/2)$, γ is the angle between the vector of the solvent dipole and the normal to the electrode surface, $\lambda = (N\downarrow - N\uparrow)/N$, N is the total number of the solvent molecules per unit surface area of electrode. In our case we set $\gamma = 0$; other quantities were estimated as follows.

On the basis of the considered model, the dependence of λ on q (Fig. 6) was calculated as

$$\ln\left[(1 + \lambda)/(1 - \lambda)\right] = -\Delta e_r - 2vq - 2e_w(\lambda - \delta)\,, \tag{11}$$

where $e_w = n_{ef}\varrho\mu_s^2/x^3kT$, $v = 4\pi\varrho\mu_s/kT$, $\Delta e_r = (E_r\downarrow - E_r\uparrow)/kT$, $E_r\downarrow - E_r\uparrow$ is the difference between the energies of interaction of the dipoles with the metal, the dipoles being oriented in two different positions at zero surface charge q. The coefficients v and e_w were obtained from the volume properties of the solvent. To find the coefficient Δe_r, we assumed that the "hump" on the curve of the differential capacity of the compact layer (C_h) corresponds to reorientation of the solvent molecules, hence $N\uparrow = N\downarrow$ ($\lambda = 0$ for $q = q_h$). The dependence of C_h on q was calculated by the Graham's method[25]; the maximum value of C_h appears at $q = 8\ \mu C/cm^2$, which corresponds to an analogous calculation according to Payne[29]. The quantity Δe_r was calculated for $\lambda = 0$ and $q = 8\ \mu C/cm^2$. It is seen from the dependence of λ on q (Fig. 6) that the DMSO molecules are at charges more negative than $8\ \mu C/cm^2$ (hence at $\lambda > 0$) in the region of adsorption of TU oriented by the positive end of the dipole toward the surface of the mercury electrode. If $X > 0$, then in accord with (*9*) the dipole moment of the adsorbed TU molecule will be larger than that of an isolated molecule. It should be noted that when the vector of the dipole deviates from the normal (γ increases), the value of X increases in accord

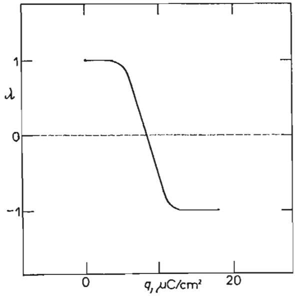

FIG. 6

Dependence of Parameter λ on Surface Charge q for Hg–DMSO Interface with the Levin–Bell's theory, and so does the effective dipole moment of the TU molecule.

We calculated from Eqs (*4*) and (*7*) the values of x_2 and ε (Table II, primed quantities) using the obtained value of the effective dipole moment of TU. It is seen that the values of x_2 derived from the model concept of Fawcett, Levine and Bell are comparable with the dimensions of the DMSO molecule. That the effective dipole moment μ_{eff} is calculated twice as large as the permanent dipole moment of TU, can be explained as follows. If we consider the adsorption of TU as a replacement of the solvent molecules with TU molecules, then for $\mu > \mu_{\text{TU}}$ the solvent will be adsorbed with the positive end of its dipole on the electrode surface; and this orientation corresponds to the Hg–DMSO interface according to the Levin–Bell's model.

This model involves therefore the replacement of the solvent molecules in the orientation predicted by the position of the "hump" on the differential capacity curves, where we have $N\downarrow = N\uparrow$. If this hump is conditioned not only by reorientation of the solvent molecules but also by disintegration of the associated solvent molecules adsorbed on the electrode surface (this was assumed in refs[30,31]), then the the theory of Levine and Bell does not permit to determine correctly the orientation of these molecules. Eq. (*9*) is still applicable, but the calculation of the true intensity of the electric field X in the compact part of the double layer is problematical.

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