

THE INFLUENCE OF THE ADSORPTION OF THIOUREA ON ELECTRODE PROCESSES AT THE MERCURY ELECTRODE

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The adsorption of thiourea at the mercury-water interface induces modifications in the state of the ionic diffuse part of the double layer, which have been studied through their influence on the apparent reaction rates of faradaic processes.

The polarographic investigation of the behavior of various depolarizers (chromate, uranyl carbonate, tetrathionate, trichloroacetate, europium(III), chromium(III), cobaltihexammine ions) leads to kinetic results which confirm the validity of the available electrocapillary data. It appears that the major role of thiourea is to shift the electrode charge density, which in turn controls the potential profile in the diffuse part of the double layer.

Protons are catalytically reduced — with an apparent rate constant which depends on both the extent of coverage by adsorbed thiourea molecules and the value of the potential.

It is known^{1,2} that the adsorption of thiourea (TU) on mercury gives capacity and electrocapillary curves which possess characteristics more akin to inorganic tensioactive anions (like SCN^- or I^-) than to the usual organic surfactants — which generally present two desorption domains — or than to aromatic compounds, for which no desorption but a tendency toward flat orientation is observed at positive charge densities of the electrode q_E .

The rather peculiar behaviour of TU has been explained³⁻⁵ by assuming (1) that the only possible steric configuration of the adsorbed molecules is the one with the dipole moment perpendicular to the surface and (2) that the extent of adsorption increases monotonously toward more positive values of q_E . As recently shown by Parsons⁵, the "composite" surface pressure curve of TU in 0.1M- KNO_3 can be correctly described by the Frumkin isotherm⁶, with an interaction parameter of 6, and a saturation coverage of 0.042 molecules/ \AA^2 (which corresponds to 24 \AA^2 for the area per adsorbed molecule). The standard free energy of adsorption for $q_E = 0$ has been found to be $-22.52 \text{ kcal mol}^{-1}$. The change of this energy with q_E has been interpreted in terms of the variation of the "average" dielectric constant of the inner layer. The fact that the various authors^{1,5} have used different supporting anions tends to complicate the intercomparison of data. It nevertheless appears⁵ that, for a given value of q_E , nitrate ions are less specifically adsorbed when thiourea is present. Since the difference depends very little on q_E or E , it seems obvious that variations in coverage by TU are not primarily responsible for the effect.

From the capacity data relative to $0.1M\text{-NaF}^I$, it is possible to obtain by graphical integration the $q_E = f(E)$ curves, and, from them, the corresponding free area $\Theta = f(E)$ (assuming $A_{TU} = 24 \text{ \AA}^2$), and the $\psi_\delta = f(E)$ curves (Fig. 1). It should be noted that the ψ_δ potentials have been simply derived from the Gouy-Chapman relation, by assuming (1) that a definite δ plan still exists, despite the heterogeneous character of the inner layer and (2) that fluoride ions are not specifically adsorbed.

In view of the remarkable simplicity of TU adsorption, and of the amount of reliable electrocapillary data which are presently available, it is of considerable interest to investigate the effect of TU on electrode reactions. It is clear that such a study is eminently apt to provide useful independent information regarding — among others — the state of the ionic diffuse part of the double-layer and the extent of coverage. Valuable data may also be expected to be obtained about the way TU controls the extent of ionic specific adsorption. Furthermore, if a sufficiently large number of reactions are examined, intercomparison may also help to detect “anormal” systems, for which there is occurrence of more specific mechanisms — like homogeneous or heterogeneous electrocatalysis brought by the surfactant molecules.

EXPERIMENTAL

Apparatus

Experiments have been performed at $25^\circ \pm 0.2 \text{ C}$, using a conventional three-electrode cell. The polarographic curves were recorded without damping circuit, at low scanning rates, with a drop time mechanically adjusted at 4.00 s. After graphical correction for the residual current (obtained separately with the supporting electrolyte containing only TU) i/i_{lim} plots of the instantaneous maximum currents were established, and the diffusion character of the limiting current was checked by the usual tests. The corresponding $\log \chi = f(E)$ curves were then constructed, using the Koutecký method⁷. When apparent rate constants were needed instead of χ values, the classical relation $\log v = \log \chi + \log \sqrt{(7D_0/12t_g)}$ was employed, with correction for the reverse reaction when total irreversibility was not achieved.

For differential capacity measurements, the so-called “tensammetric” method has been used. A small A.C signal (117 Hz 30 mV) was superimposed on the ramp potential, the D.C. generator being shunted by a large capacitor. The resulting A.C current was fed to a frequency-selective amplifier (A. O. I. P. RL 40), detected and recorded at the maximum size of the drop (4.00 s). The deflections of the recorder were calibrated immediately before and after any run by substitution with an equivalent series R—C circuit, in which resistance was equalized to the effective cell resistance for $t_g = 4.00 \text{ s}$ (a value measured at 100 kHz) and the capacity was a precision decade capacitor. Intercomparison between the results obtained with this technique and available accurate data found in the literature did not reveal any significant discrepancy. The overall precision of the instrument, of the order of 1%, was judged sufficient for the limited purposes of that part of the research. Surfactant concentrations were generally so large that correction for mass transfer was not needed.

Material

Triply distilled water and doubly distilled mercury were used. Standard procedures have been used to determine the concentration of the reagents. The various supporting electrolytes were

prepared from A.R. products (after recrystallisation, when it appeared desirable, and calcination, each time it was practicable). The depolarizers were generally used without further purification. Merck "chromatography grade" thiourea has been used, after recrystallisation from ethanol.

RESULTS

ADSORPTION DATA

Accurate differential capacity values are already available for variable concentrations of TU in 1M-NaF¹ and 0.1M-NaNO₃⁵. In order to extend the range of compositions and concentrations for subsequent analysis of the kinetic data, a few additional capacity-potential curves have been collected, using the tensammetric technique, for the following solutions [TU] = 0.25; [NaF], [NaNO₃], [NaClO₄] 0.9; [NaF], [NaClO₄] 0.1 mol/l.

Fig. 2. shows conclusively that increasing the salt concentration enhances the hump and that, for a given ionic strength, the order is F⁻ < ClO₄⁻ < NO₃⁻ (in the case

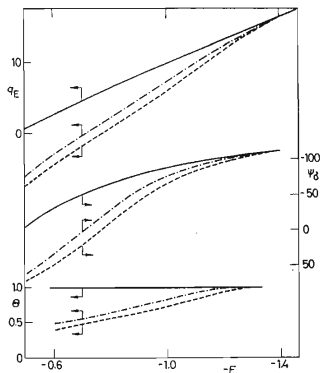


FIG. 1

Effect of TU Concentration and Electrode Potential (E (s.c.e.), V) on the Electrode Charge Density q_E ($\mu\text{C}/\text{cm}^2$), the ψ_δ potential (mV) and the Extent of Free Area θ 0.1M-NaF, [TU]: ——— 0, - - - - 0.1, - · - · 0.25 mol/l.

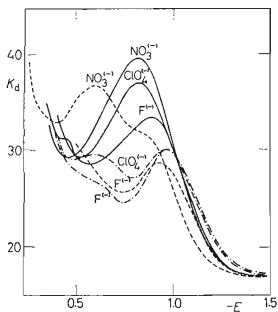


FIG. 2

Capacity K_d ($\mu\text{F cm}^{-2}$) versus Potential E (V (s.c.e.)) Curves for Various Compositions

— [NaX] = 0.9, [TU] = 0.25; - - - [NaX] = 0.1; [TU] = 0.25; ····· [NaX] = 0.1, [TU] = 0.1 mol/l.

of 0.9M solutions, it should be born in mind that salting-out may act as a second-order factor).

When these curves are compared with the corresponding ones with no TU, it appears that the position of the hump tends to be determined more by q_E than by E itself. Table I gives selected values of q_E , obtained by the usual procedure of graphical integration of the capacity curves, using as integration constants values of q_E available at -1.5 V (S.C.E.).

It is noteworthy that, in presence of strongly adsorbed anions (like halide ions), the capacity-potential curve exhibits a very peculiar shape, (see Fig. 11A) with a characteristic narrow peak, corresponding to a sudden drastic modification of the superficial structure, which is also reflected by sharp discontinuities in the Tafel lines of electrode reactions (see later).

TABLE I
Values of the Charge Density q_E ($\mu\text{C}/\text{cm}^2$) in the Presence of Thiourea (TU)

$-V$ (S.C.E.), V	[NaX] = 0.9, [TU] = 0.25			[NaX] = 0.1, [TU] = 0.25		[NaX] = 0.1, [TU] = 0.1	
	F^-	NO_3^-	ClO_4^-	F^{-a}	ClO_4^-	F^-	NO_3^{-b}
0.4	+ 6.3	+12.6	+12.0				+11.5
0.6	+ 0.9	+ 6.6	+ 5.8	+ 4.5	+ 5.3	+ 3.4	+ 4.4
0.8	- 4.6	- 0.8	- 1.2	- 0.5	- 0.5	- 2.1	- 2.5
1.0	- 9.3	- 8.0	- 7.9	- 5.8	- 5.8	- 7.0	- 8.3
1.2	-13.4	-12.7	-12.7	-10.8	-10.8	-11.6	-12.6
1.4	-16.5	-16.3	-16.2	-15.0	-15.0	-16.2	-16.2

^a Calculated from data of ref.¹; ^b calculated from data of ref.⁵.

KINETIC DATA

Choice of the Depolarizers

The various depolarizers which have been studied (chromate, uranylcarbonate, tetrathionate, trichloroacetate, protons, europium(III), chromium(III), cobalt-hexammine) have been selected in order to meet the following requirements: 1. electron transfer as rate-determining step 2. kinetic parameters known by previous works 3. absence of significant specific adsorption 4. no chemical interaction with TU

5. rate constants measurable in the potential range of interest (roughly from -0.4 V up to -1.4 V (s.c.e.)) 6. largest spectrum of effective electronic charge z_B .

Table II summarizes some data of interest, pertaining to the depolarizers which have been employed⁸.

TABLE II
Effective Charges Z_B , Charge Transfer Coefficients α and Half-Wave Potentials $E_{1/2}$

Depolarizer	Z_B	α	$-E_{1/2}$	Medium used in this work
$\text{Cl}_3\text{C}-\text{COO}^-$	-1	0.19	1.38	0.1M-NaF 0.1M-NaClO ₄
CrO_4^{2-}	-2	0.6	0.99	2 . 10 ⁻² M-NaOH 8 . 10 ⁻² M-NaF 2 . 10 ⁻² M-NaOH 2 . 10 ⁻² M-NaOH 8 . 10 ⁻² M-NaClO ₄
S_4O_6	-2	0.19	1.37	0.1M-NaClO ₄
$\text{UO}_2(\text{CO}_3)_3^{4-}$	-2	0.55	1.23	0.1M-Na ₂ CO ₃
H_3O^+	+1	0.52	1.53	1M-NaClO ₄
Eu^{3+}	+2	0.38	0.65	0.1M-NaClO ₄ 2 . 10 ⁻⁴ M-HClO ₄
Cr^{3+}	+2	0.41	0.74	10 ⁻³ M-HClO ₄ 0.099M-NaClO ₄
$\text{Co}(\text{NH}_3)_6^{3+}$	+2	0.78	0.28	10 ⁻² M-HClO ₄ 9 . 10 ⁻² M-NaClO ₄ 10 ⁻² M-HClO ₄ 9 . 10 ⁻² M-NaF

General Trends

As expected, the addition of TU distorts the Tafel lines, the order of magnitude of the effect increasing with the concentration of TU at a given potential, and toward positive potentials at constant concentration of TU. The reduction of anions is enhanced the more the larger their negative electronic charge, in contrast with cations which show the opposite trend (with the notable exception of H_3O^+).

Fig. 3 and 4 illustrate a typical behavior (trichloroacetate ion), respectively at variable TU concentration and constant J , and *vice versa*. When the ionic strength is varied, all the Tafel curves are practically coincident at -0.75 V (s.c.e.), which is obviously close to the point of zero charge.

In some cases (chromate, uranyl carbonate) the extent of acceleration is such that the initial part of the polarographic curves corresponds to a reversible behavior.

Intercomparison of the Apparent Rate Constants before and after Addition of a Standard Amount of Surfactant

The variations in rate constants brought up by the addition of 0.25M-TU have been converted into corresponding changes $\Delta\psi'_8$ of the ψ_8 potentials, by using the Frumkin

relation, and assuming that the reaction proceeds only on the free area Θ of the electrode.

Accordingly

$$\Delta\psi'_\delta = - \frac{\varphi_e}{(z_B - \alpha) RT} \Delta \ln \frac{v(0.25M-TU)}{\Theta v(0M-TU)}$$

Using the Gouy-Chapman ψ_δ values relative to the solutions free from TU, one has

$$\psi'_\delta(0.25M-TU) = \psi_\delta^{G-Ch}(0M-TU) + \Delta\psi'_\delta$$

Each depolarizer allows to construct a $[\psi'_\delta = f(E)]_{0.25M-TU}$ curve. These curves can be compared (Fig. 5) with the corresponding $\psi_\delta = f(E)$ curves directly calculated from $q_E(0.25M-TU)$ (Fig. 1). Inspection of Fig. 5 indicates (again with the notable exception of the hydrogen ions — a case which will be reconsidered later) that for all the depolarizers, the calculated ψ'_δ values show the correct polarity and a satisfactory order of magnitude. They are reasonably self-consistent, and in good agreement with the thermodynamic values. The obvious conclusion is that the kinetic effect exerted by TU is mostly a ψ effect, determined the by change in q_E brought by its specific adsorption. Since the correction made for surface coverage gives a better grouping of the curves, it is clear that blocking is the other determining factor. (It should be

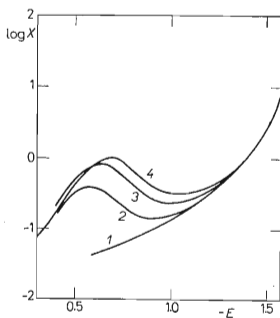


FIG. 3

Effect of TU Concentration on the Polarographic Reduction of the Trichloroacetate Ion

0.1M-NaClO₄, [TU] 1 0, 2 0.03, 3 0.1, 4 0.25 mol/l, E in V (s.c.e.).

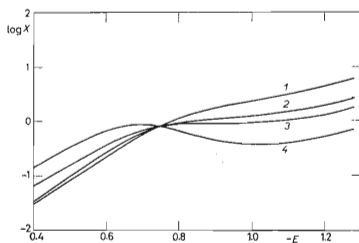


FIG. 4

Effect of Ionic Strength on the Polarographic Reduction of the Trichloroacetate Ion

$10^{-3}M-Cl_3C-COO^-$, 0.25M-TU, [Na.
.ClO₄]: 1 1, 2 0.5, 3 0.3, 4 0.1; E in V (s.c.e.).

stressed however, that the apparent rate constant is probably not a simple function of the free surface, at the high coverages, since steric hindrance may then become significant.)

Behavior in 0.1M-NaF

The preceding intercomparison suffers to some extent from the circumstance that the supporting electrolytes (and more particularly the anions) were not identical for all the systems (see Table II) a fact which may be partially responsible for the scattering in ψ'_δ potentials.

Using a limited number of systems (selected as giving the most reliable $\Delta\psi'_\delta$ values), experiments have been conducted in 0.1M-NaF (Fig. 6), in order to obtain information directly comparable to the preexisting thermodynamic data (Fig. 1).

As shown in Fig. 7, correcting the ψ_δ base line (for 0.1-NaF without TU — upper curve) for the “average” $\Delta\psi'_\delta$ potentials induced by TU adsorption (lower curve) gives a ψ'_δ line which is in excellent agreement with the corresponding ψ_δ values derived from the data of Schapink and coworkers¹.

This fact reconfirms that the major role played by TU is to modify, for a given potential, the state of the adjacent ionic diffuse layer.

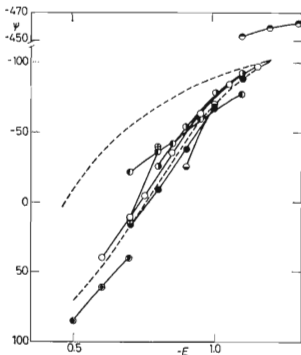


FIG. 5
Effect of TU Concentration on Various Electrode Reactions (see text)

E in V (s.c.e.), ψ in mV, ——— ψ'_δ , - - - ψ_δ , $[\text{Na}^+] = 0.1 \text{ mol/l}$, $[\text{TU}] = 0, 0.25$, respectively.

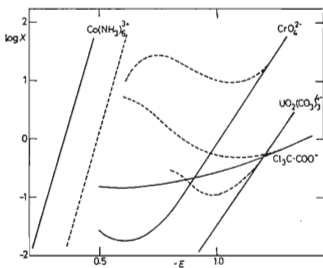


FIG. 6
Effect of Addition of TU on Various Electrode Reactions in Fluoride Medium

— 0.1M-NaF, - - - 0.1M-NaF + 0.25M-TU. E in V (s.c.e.), $\log \chi$ corrected for θ .

TABLE III
Charge Densities q_i ($\mu\text{C}/\text{cm}^2$) and Surface Concentrations of ClO_4^- Ions $\Gamma_{\text{ClO}_4^-}$ ($\mu\text{C}/\text{cm}^2$)

V (S.C.E.), V	$q_{\text{F}^-, \text{TU}}$	$q_{\text{ClO}_4^-, \text{TU}}$	$\Gamma_{\text{ClO}_4^-, \text{TU}}$	$\Gamma_{\text{ClO}_4^-}$
0.5	+ 7.6	+ 8.6	+ 3.7	+ 5.7
0.6	+ 4.5	+ 5.3	+ 2.9	+ 4.2
0.7	+ 2.0	+ 2.4	+ 2.0	+ 3.7
0.8	- 0.5	- 0.3	+ 1.4	+ 2.1
0.9	- 22.9	- 2.9	+ 1.1	+ 1.1

The Effect of TU on the Adsorption of Weakly Adsorbable Anions

As shown by Parsons⁵, the adsorption of TU seems to decrease the superficial excess of nitrate ions, at constant q_E measurements of that nature are tedious and difficult. Using depolarizers as probes, the following kinetic method may be used as a substitute: a) for a serie of given electrode potentials, the electrode charge densities

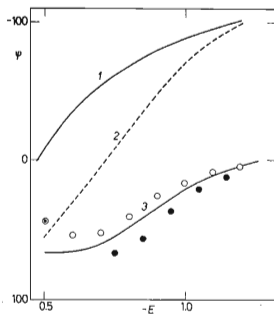


FIG. 7

Intercomparison between ψ_δ Potentials (mV) Calculated from Kinetic (dotted line) and Thermodynamic (O) Data

1 ψ_δ , 0.1M-NaF, Gouy and Chapman,
2 ψ'_δ , 0.1M-NaF + 0.25M-TU, ψ_δ from ref.¹,
3 $\Delta\psi'_\delta$, Frumkin. E mV (S.C.E.).

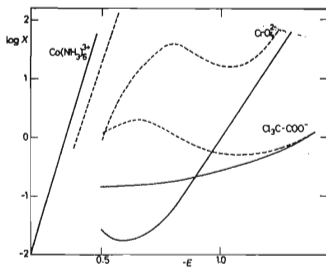


FIG. 8

Anion Effect in the Presence of TU for Various Electrode Reactions (see text)

— 0.1M-NaF, - - - 0.1M-NaClO₄ + 0.25M-TU, log χ corrected for Θ , E in V (S.C.E.).

$q_E(X^-, TU)$ and $q_E(F^-, TU)$ are determined by integration of the corresponding capacity curves; b) for the same potentials, the change $\psi'_\delta(X^-, TU) - \psi'_\delta(F^-)$ is calculated from rate constant measurements, c) Assuming that fluoride is not specifically adsorbed at all, and combining the Gouy-Chapman and the Frumkin theories, it is easy to compute the charge $\eta(X^-, TU)$ of the diffuse part of the double layer. d) $q_E(X^-, TU) + \eta(X^-, TU)$ finally gives $q_i(X^-)$, the amount of specifically adsorbed anions — a quantity which can be conveniently plotted in function of $q_E(X^-, TU)$ itself.

The reliability of this method obviously depends on the validity of the Gouy-Chapman and Frumkin theories, and is critically dependent upon the choice of the depolarizers — which must act as far as possible as “non-disturbing” and “non-disturbed” probes. As shown in a recent work, however, superficial excesses for Cs^+ obtained by this method⁸ are in excellent agreement with recent electrocapillary data⁹ an *a posteriori* confirmation of its intrinsic value.

Coadsorption of TU and perchlorate ions. From kinetic results obtained with trichloroacetate, chromate and cobaltihexammine ions as probes (Fig. 8), “average” ψ'_δ potentials have been evaluated (Fig. 9), from which q_i have been calculated.

Intercomparison with thermodynamic data gathered by Payne¹⁰ (Fig. 10) shows that, for the same values of q_E , the extent of specific adsorption of the perchlorate ion decreases when TU is coadsorbed.

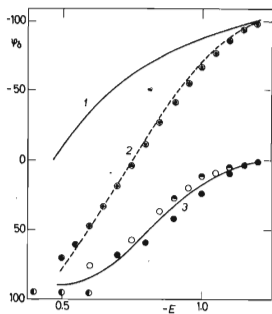


FIG. 9

Evaluation of ψ'_δ (mV) in the Presence of the Perchlorate Ion

1 ψ'_δ , 0.1M-NaF, 2 ψ'_δ 0.1M-NaClO₄ + 0.25M-TU, 3 $\Delta\psi'_\delta$ Frumkin, E in V (s.c.e.).

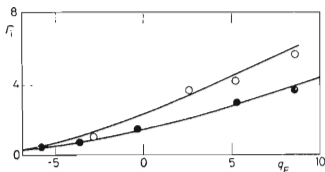


FIG. 10

Specific Adsorption of Perchlorate in absence (○, Payne) and in the presence (●, this work) of 0.25M-TU

0.1M-ClO₄⁻, τ_i and q_E in $\mu C/cm^2$.

The same type of experiments, performed in 0.1M nitrate solutions indicates that the nitrate ion tends also to be desorbed by TU, at constant q_E , with lowering in specific superficial excesses in fair agreement with the data presented by Payne¹³ (Table IV).

TABLE IV
Specific Adsorption of the Nitrate Ion

q_E	q_i^a	q_i^b
0.0	3.0	0.9
+2.5	5.0	2.5
+5.0	7.8	4.3
+7.5	10.3	6.4

^a Taken from Fig. 3 of ref. ¹³ (no TU); ^b values found in this work (TU 0.1M).

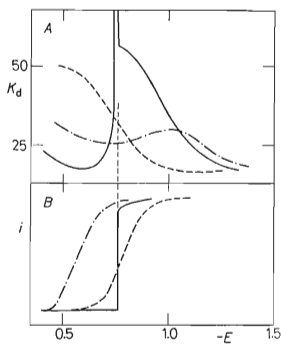


FIG. 11

Effect of Bromide Ions on the Behaviour of TU

A Differential capacity K_d (μF), B reduction current i of CrO_4^{2-} . - · - · - 0.25M-TU + 0.1M-NaF, - - - 1M-NaBr, ——— 1M-NaBr + 0.25M-TU. E in V (s.c.e.).

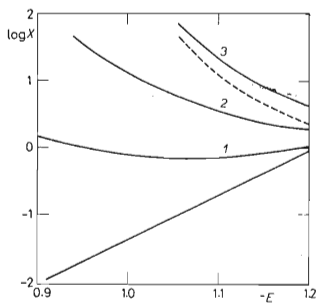


FIG. 12

Synergetic Effect of TU and Tl on Chromate Reduction

$10^{-3}\text{M-CrO}_4^{2-} + 2 \cdot 10^{-2}\text{M-NaOH}$, 1 + 0.25M-TU, 2 + 1.5% Tl, 3 + 0.25M-TU + 1.5% Tl. Base line corresponds to mercury, dotted line is the algebraic sum of 1 and 2. E in V (s.c.e.).

Behavior of TU in Presence of Very Tensioactive Anions

In presence of halide ions, the capacity-potential curves present an unexpected shape. Starting from negative potentials, the curve rises much more rapidly than usually, develops a rather sharp maximum, and drops afterwards to very low values. That the peak is related to a considerable change in the superficial structure is demonstrated by the corresponding behavior of depolarizers. Examination of Fig. 11 (which shows as typical example the behavior of 0.25M-TU in 1M-NaBr, with CrO_4^{2-} as probe) shows that at potentials more negative than the peak, TU adsorption significantly prevails over that of Br^- (as reflected by the enhancement of the reduction rate of CrO_4^{2-}), contrary to the situation on the other side of the peak, where strong inhibition indicates either extensive increase in Br^- adsorption, or, more likely, the synergetic built-up of a very compact two-dimensional composite layer.

Extensive work is now under progress in order to gain quantitative information about the various superficial excesses involved and to understand the detailed structure. It is of interest to note incidentally that TU may be completely expelled from the inner layer by the presence of more tensioactive heterocyclic compounds (*e.g.* quinoline) which assume flat adsorption stabilized by *H*-bonding interactions with the surface.

Behavior of TU on Thallium Amalgams

Thallium amalgams and mercury with TU adsorption present a strikingly similar behavior¹¹. In both cases, at increasing concentration of TU or Tl, the potential of zero charge is shifted toward more negative values, and the ψ_δ potentials are rendered more positive (the magnitude of the latter effect increasing toward less negative electrode potentials). If the adsorption of TU is assumed to be chiefly controlled by q_E , it can be predicted that, at constant potential, its superficial excess will increase with the amalgam concentration (of course as far as the field exerted by the surfactant molecules is not disturbing the effect of the thallium itself — which is to induce specific adsorption of amalgam-free mercury at the interface). Since both TU and Tl contribute to shifting ψ_δ toward less negative (or more positive) values, electrode reactions can be expected to be affected by an unusually large ψ effect, of synergetic nature. Results obtained with various depolarizers,¹² at variable concentrations TU and Tl, indicate that this is indeed generally the case. A typical example is afforded by the reduction of the chromate ion (Fig. 12) for which the increase in $\Delta \log \chi$ caused by the simultaneous presence of Tl and TU is larger than the sum of the two separate effects.

The simultaneous presence of TU, Tl and a tensioactive cation (like Cs^+ or tetramethylammonium) induce ψ_δ potentials which are still considerably less negative — with corresponding larger effects on electrode kinetics.

Mechanism of Reduction of the Hydrogen Ions

As already stated (see also Fig. 5), the effect of TU on H_3O^+ reduction cannot be explained in terms of the ψ mechanism common to all the other systems: the rate constants are indeed enhanced, instead of the expected decrease. Experiments have been carried out in 1M-NaClO_4 . For $[\text{H}_3\text{O}^+] = 4 \cdot 10^{-3} \text{ mol/l}$, $[\text{TU}]$ has been explored from 0 up to 0.45 mol/l (Fig. 13).

In another serie at constant $[\text{TU}] 0.25 \text{ mol/l}$, $[\text{H}_3\text{O}^+]$ has been varied from $5 \cdot 10^{-4}$ to $5 \cdot 10^2 \text{ ml/l}$.

As shown by Fig. 13, the overvoltages start to decrease, as soon as the concentration of TU exceeds a threshold value of the order of 10^{-4} mol/l . The effect is important: at a given potential, the apparent rate constants may increase by more than three orders of magnitude. At very high TU concentrations, the slopes $d \log \gamma/dE$ tend to be somewhat steeper (larger apparent α coefficient). At constant TU concentration, the apparent rate constants for a given potential are essentially pH-independent (order 1). Experiments performed with TU using an eudiometer cell show that hydrogen is essentially the reaction product.

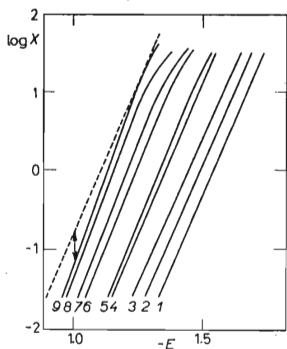


FIG. 13

Effect of TU Concentration on the Tafel Plots for Reduction of Hydrogen Ions

$10^{-3}\text{M-H}_3\text{O}^+$, 1M-NaClO_4 , TU: 1 0, $2.5 \cdot 10^{-4}$, $3 \cdot 10^{-3}$, $4.5 \cdot 10^{-3}$, $5 \cdot 10^{-2}$, $6.5 \cdot 10^{-2}$, $7 \cdot 10^{-1}$, $8.25 \cdot 10^{-1}$, $9.45 \cdot 10^{-1} \text{ mol/l}$. E in V (s.c.e.).

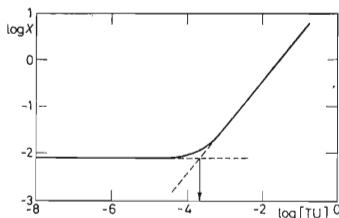


FIG. 14

Effect of TU Concentration on the Rate Constants for Reduction of Hydrogen Ions at -1.25 V (s.c.e.)

$1\text{M-NaClO}_4 + 4 \cdot 10^{-3}\text{M-H}_3\text{O}^+$.

Since no prewaves are observed (which should indicate that a bulk prior reaction is the controlling step), it can be deduced that the rate-determining step is the electron-transfer, assisted by the adsorbed surfactant molecules.

Strictly speaking, the net current is always the sum of the two contributions due to the "normal" and the "catalytic" paths. However, TU concentration for which mechanisms are both significant is restricted to the range $5 \cdot 10^{-4} - 5 \cdot 10^{-3}$ mol/l. (For such low concentrations mass transfer of TU toward the surface can no longer be neglected; this complication however hardly affects the proposed mechanism, which is based on the behavior observed at higher concentrations.)

From the bilogarithmic rate constant - TU concentration plot (Fig. 14), it appears that the two processes have equal rate constants for $[TU] \approx 2 \cdot 10^{-4}$ mol/l.

When TU concentration is large enough to render both the effects of the normal part and of the mass transfer of the surfactant negligible, the rate-constants are satisfactorily expressed by the following general equation

$$v_{\text{H}_2\text{O}^+} = k_{0\text{M-TU}}(1 - \Theta) \exp \left[-\frac{\alpha F}{RT} (E - E_0) \right] \exp \left[-\frac{(1 - \alpha) F}{RT} \psi_s \right] \quad (\text{for } \Theta \approx 1).$$

with

$$k_{0, \text{TU}} = 10^{-13.5} \text{ cm s}^{-1}, \quad \alpha = 0.50 \quad (\text{s.c.E. scale})$$

At sufficiently negative potentials, the limiting Henry isotherm is obeyed and ψ_s variations are negligible. The apparent rate constants are thus directly proportionnal to the concentration of TU.

At less negative potentials, and high TU concentration, the Frumkin isotherm prevails, and the Henry approximation is no longer valid (At -1.0 V (s.c.E.) and $[TU] = 0.45$ mol/l, this brings a correction factor $\Delta \ln v$ of about -0.18). Simultaneously, the variation of ψ_s with $[TU]$ becomes significant (≈ 20 mV). Both effects are cumulative: for the given conditions, they should theoretically decrease the apparent rate constant (from its linearly extrapolated log value) by a factor $\Delta \log \chi$ of about -0.35 . Taking this correction into account, it is possible to reconstruct a hypothetical Tafel line (dotted line of Fig. 13) which is less steeper, and presents the same slope as one observes at more negative potentials.

Comparison with the rate expression for hydrogen evolution in absence of TU, indicates that rate constant on covered area is increased by a factor of about $10^{3.5}$. This enhancement is obviously caused by the well-known catalytic effect of sulphur-containing compounds, very commonly observed at the dropping mercury electrode. Additional experiments - now under progress - have been made with various substituted thioureas (methyl-TU, ethyl-TU, dimethyl-TU, phenyl-TU *etc.*). Typical Tafel plots (Fig. 15) indicate that, at constant bulk concentration, the catalytic action increases with the molecular weight of the surfactant. It seems however

likely that the "intrinsic" catalytic power of these compounds is basically the same, and that the observed variations mostly reflect differences in adsorbability (Traube rule).

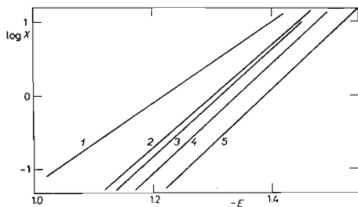


FIG. 15

Effect of Various TU Derivatives on the Tafel Plots for Reduction of Hydrogen Ions
1 Phenyl TU, 2 2-methyl TU, 3 ethyl TU, 4 methyl TU, 5 TU. E in V (s.c.e.).

CONCLUSIONS

With the obvious exception of depolarizers which are either complexed or catalytically reduced by thiourea, the influence of this surfactant on electrode reactions can be satisfactorily ascribed to its simultaneous action on the diffuse part of the double layer, and on the extent of free surface.

The fact that the observed variations in rate constants can be quite accurately predicted on the simple basis of the Frumkin and Gouy-Chapman theories indicates that the thiourea adsorption essentially affects the electrode charge-density, which in turn controls the structure of the ionic double layer.

There is no convincing evidence that the presence of the surfactant alters by itself the prevailing local water structure. It should however be mentioned that the fact that structure-destroying anions like nitrate or perchlorate are less adsorbed when thiourea is present may indicate that thiourea is somewhat acting as a local structure-maker, able to expulse to a certain extent incompatible structure-destroying ions (under this line, it is perhaps relevant to note that the reduction of the hydrophobic tetrathionate ion is less enhanced than it should be expected). Thiourea may be conveniently used to modify the diffuse double-layer structure, while maintaining both electrode potential and ionic composition constant — a possibility also afforded by some amalgams. This circumstance constitutes by itself a useful diagnosis criterion, in order to evaluate to what extent the electron-transfer step is or not preceded by a fast ion-pairing reaction.

It must be stressed that the influence of thiourea on electrode kinetics is intrinsically different from the usual behavior displayed by other surfactants — which mostly inhibit reactions by blocking the electrode surface. This difference reflects that thiourea molecules can only assume a covalency-induced “rigid” orientation, at any potential or coverage, in contrast with the other “soft” surfactants, which are merely obeying the imposed electrical field, by modifying their average orientation, taking which also depends their interactions with the solvent and between themselves.

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