

DC POLAROGRAPHIC DETERMINATION OF SURFACTANTS

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The minimum on the polarographic curves for Bi(III) reduction in HCl solutions occurring when small amounts of surfactants are present can be used for their quantitative determination. The form of the polarograms was examined with respect to the concentration of the surfactant, and the range of concentrations in which the method of determination can be used is discussed.

Quantitative determination of surfactants in aqueous medium by electroanalytical methods has recently been the subject of several communications¹⁻³. The diminishing of the polarographic current corresponding to reduction of Bi(III) in 1M-HCl as the concentration of added surfactant increases can also be utilized in this respect. The present work deals with the influence of a surfactant on the reduction process of Bi(III) at the dropping Hg electrode with respect to its applicability to the quantitative determination of detergents. Sodium dodecylsulphonate (SDS) was chosen as model substance because of its stability in aqueous solutions. However, the results are applicable to many other surfactants.

EXPERIMENTAL

All the reagents used were of reagent grade. Water was distilled from alkaline KMnO₄ solution and then redistilled. Mercury was purified chemically and thrice vacuum-distilled. Oxygen was removed from the solutions by bubbling argon (purity grade at least 99.96%).

Two solutions of bismuth nitrate were prepared in HCl medium, the first being 1 mmol l⁻¹ in Bi(III) and 1 mol l⁻¹ in acid. The second contained moreover 5 mmol l⁻¹ SDS. The concentration of bismuth was also checked by titrating with EDTA in the presence of xylenol orange as indicator⁴. Solutions of 1 mmol l⁻¹ Bi(III) + 0–5 · 10⁻³ mol l⁻¹ SDS in 1 mol l⁻¹ HCl were obtained by adding the appropriate amounts of both solutions.

The *i*-*E* curves were recorded with an EG and G Princeton Applied Research polarographic analyzer, model 174A, combined with a model RE0074 X-Y recorder of the same manufacturer. The working cell was of the conventional type with space for a calomel reference electrode saturated in NaCl (SCE), a dropping Hg electrode (DME), and a Hg pool counter-electrode with a Pt contact. The drop time was 2 s at a rate of flow of mercury 0.86 mg/s. The temperature of the solutions was maintained at 25 ± 0.1°C. The polarogram of the solution with electroactive species was recorded along with that of the base electrolyte. The latter corresponds to the residual or charging current, which was subtracted from the polarographic diffusion current.

RESULTS AND DISCUSSION

Adsorption of surfactant molecules at the surface of the DME has an inhibiting effect on the electrode process (*i.e.* Bi(III) reduction), causing a minimum in the diffusion current when the polarographic waves develop at more positive potentials than the zero charge potential.

The polarogram of a solution of 0.001M-Bi(III) + 1M-HCl presents⁵ a maximum of the first kind around -0.1 V. The limiting diffusion current, i_d , is attained around -0.15 V, passes through a minimum, and is recovered again around -1.0 V, shortly before the reduction wave of H^+ ions (Fig. 1, curve 1 and Fig. 2, curve 1).

Addition of SDS causes marked changes of the polarographic waves: the height of the maximum decreases, the rest of the curve presenting a more regular form (Fig. 2, curves 2 and 3). Further additions of the surface active agent continue to lower the maximum giving rise to the formation of a minimum on the limiting current situated at high negative potentials with regard to the half-wave potential (Figs 1 and 2). The maximum disappears completely at concentrations of SDS above 0.13 mmol l^{-1} (Fig. 2, curves 2–7).

Higher concentrations of the surfactant cause an increase in the depth of the minimum (Fig. 1, curves 2–12) until a "saturation" concentration of SDS around 0.6 mmol l^{-1} is reached, further additions having no effect on the minimum (Fig. 1, curves 12–17).

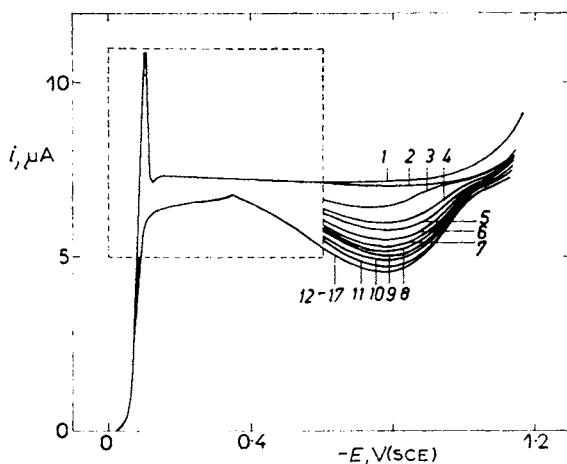


FIG. 1

Polarographic curves for reduction of Bi^{3+} . Solution of 0.001M- Bi^{3+} in 1.0M-HCl; concentration of SDS in millimoles per liter: 1 0; 2 0.087; 3 0.099; 4 0.127; 5 0.147; 6 0.177; 7 0.196; 8 0.227; 9 0.245; 10 0.302; 11 0.398; 12 0.591; 13 0.976; 14 1.457; 15 2.00; 16 2.75; 17 5.00

On the other hand, the current also decreases in the region of the most positive potentials of the i - E curve, a characteristic potential existing between this part of the curve and the minimum for each concentration of SDS at which the current tends to attain a limiting value giving rise to a small secondary maximum (Fig. 2, curves 13–19).

The effect of the surfactant on the i - E curve diminishes as the concentration, x , of Cl^- ions decreases in the solution of x M-HCl + $(1 - x)$ M- HClO_4 . Reduction of Bi(III) is not inhibited by adsorption of SDS in 1M- HClO_4 (ref.⁶).

The reduction of Bi(III) at the Hg electrode in the presence of HCl has also been shown to be catalysed by adsorbed Cl^- ions (bridge effect)⁶. The presence of a surfactant such as SDS affects the polarographic wave in the region in which it is adsorbed on the Hg electrode. The diminishing of the polarographic current (which appears in the potential region where the real part of the faradaic impedance is negative⁶) begins at about -0.2 V; at this potential the SDS starts to be adsorbed causing inhibition of the electrode process.

Adsorption of SDS

Interpretation of the effect of SDS on the reduction of Bi(III) in the presence of Cl^- ions requires knowledge of the way in which the SDS is adsorbed on the Hg elec-

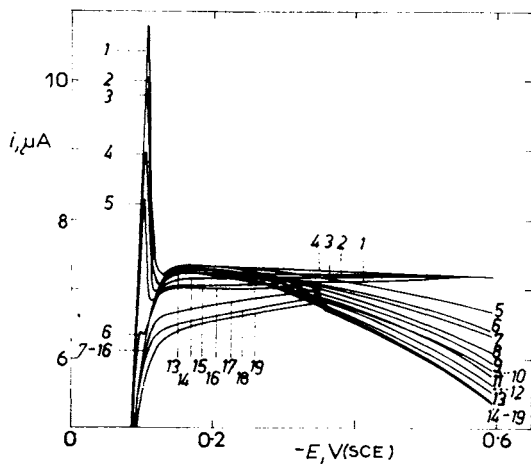


FIG. 2

Extension of square marked in Fig. 1. Portion of the polarograms for 1M-HCl + 0.001M- Bi^{3+} ; concentration of SDS in millimoles per liter: 1 0; 2 0.002; 3 0.005–0.050; 4 0.087; 5 0.099; 6 0.127; 7 0.147; 8 0.177; 9 0.196; 10 0.227; 11 0.245; 12 0.302; 13 0.398; 14 0.591; 15 0.976; 16 1.45; 17 2.00; 18 2.75; 19 5.00

trode. To this end, the adsorption of SDS in 0.1M-NaClO₄ was studied⁷. The choice of this supporting electrolyte for comparison of the results with those for the system 0.001M-Bi(III) + 1M-HCl is justified by the analysis of the differential capacity curves obtained in both media^{5,7}. Comparison of the afore-mentioned curves revealed that the controlling factor is adsorption of SDS and not the supporting electrolyte employed.

Fig. 3 shows the dependences of the surface excess of SDS, Γ , in NaClO₄ solution on the potential at various concentrations of the surfactant. The values of Γ are indeed higher than those obtained for other compounds⁸. This can, however, be attributed to the formation of condensed films at the interface.

The polarographic saturation concentration of SDS (Fig. 1) is approximately 0.6 mmol l⁻¹ at potentials more negative than 0.3 V. However, Fig. 3 implies a higher saturation concentration being a function of the potential with a value of around 1 mmol l⁻¹ SDS at the potential of the current minimum (-0.77 V).

It is thus demonstrated that no exact correlation exists between the total quantity of surfactant adsorbed and its effect on the polarographic reduction of Bi(III) in HCl solution.

It was also shown^{7,9,10} that the SDS molecules are adsorbed at different orientations depending on their concentration and on the potential. It is possible that only a certain orientation of the adsorbed SDS molecules is effective in inhibiting the electrode process.

The overall SDS adsorption can be decomposed into three specific adsorptions giving rise to three families of Γ - E curves (Fig. 4). It was shown¹² that the first and

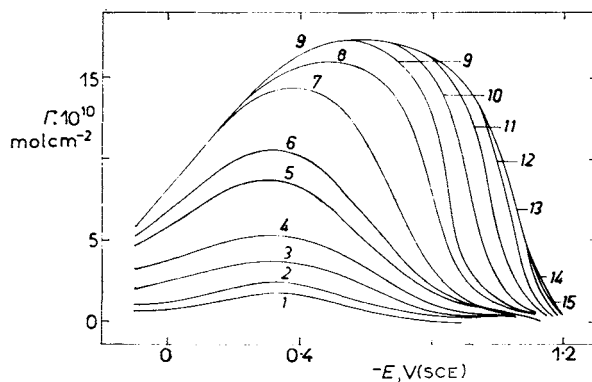


FIG. 3

Surface excess of SDS against potential. Concentration of SDS in millimoles per liter: 1 0.1; 2 0.2; 3 0.3; 4 0.4; 5 0.5; 6 0.525; 7 0.6; 8 0.7; 9 0.725; 10 0.85; 11 0.9; 12 1.025; 13 1.2; 14 1.5; 15 2.5. From electrocapillary measurements⁸

third forms of adsorption (orientation of the surfactant parallel to the electrode and formation of micelles, respectively) do not inhibit the electrode process.

It is, therefore, the second form of adsorption of SDS, involving perpendicular orientation of the molecules on the electrode surface, which really inhibits the electrode process. A detailed description of these ideas is given in ref.¹¹.

The curve of $1 - \Theta_2$ as function of potential E ($\Theta_2 = \Gamma_2/\Gamma_{2s}$ is the relative surface coverage corresponding to the second isotherm) and the curve of i/i_d as function of E (i_d is the limiting diffusion current) have a similar form. The shifts observed are due to the Frumkin effect, among other causes, and to the formation of micelles that takes place at $C_{\text{SDS}} \geq 0.6 \text{ mmol l}^{-1}$ (ref.¹¹).

These facts indicate that the "blocking effect" is the main inhibitory effect of the surfactant on the polarographic reduction of Bi(III) in the presence of Cl^- ions.

Fig. 5 shows the polarographic i - E curve corresponding to $C_{\text{SDS}} = 0.6 \text{ mmol l}^{-1}$, together with the curve calculated from the equation

$$i = i_d(1 - \Theta_2) \quad (1)$$

on the assumption that the only effect of adsorption on the reduction of Bi(III) is the diminishing of the free surface area.

It was shown^{10,11} that the Frumkin effect is also responsible for the shift of the $(1 - \Theta_2)$ - E curve by 50 mV to more positive potentials. This fact, together with

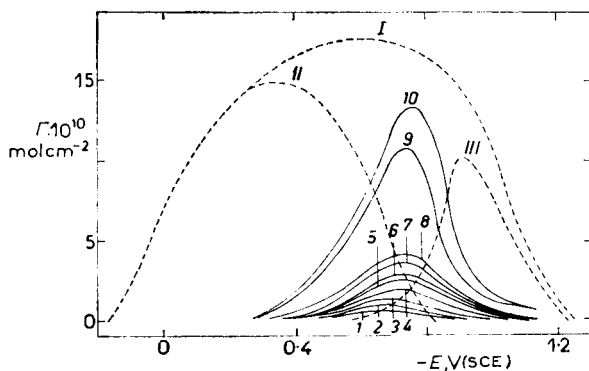


FIG. 4

Surface excess of SDS against potential. Full lines show adsorption of SDS with molecules orientated normal to the Hg electrode. Concentration of SDS in millimoles per liter: 1 0.1; 2 0.2; 3 0.3; 4 0.4; 5 0.5; 6 0.525; 7 0.6; 8 0.625; 9 0.7; 10 0.725. Dashed lines: I Plot of limiting surface excess of SDS against potential (Γ_s - E curve); II plot of Γ_s against E corresponding to the first isotherm (Γ_{1s} - E); III plot of Γ_s against E corresponding to the third isotherm (Γ_{3s} - E)

the previous one, permits the d.c. polarogram to be calculated with an error of 5% inherent in the calculation (Fig. 5).

Analytical Application

Based on the fact that the depth of the polarographic minimum depends on the concentration of surfactant present in the solution, the possibility of using such a correlation in the determination of surfactants was considered. The method does not require preconcentration or adsorptive accumulation of the surfactant as in other electrochemical methods (*e.g.* stripping voltammetry¹), nor does the electrode have to equilibrate for several minutes in the solution with the risk of other impurities also being adsorbed.

Fig. 6 represents a calibration curve. The minimum current for an unknown solution of surfactant can be compared with this curve and the concentration can be read directly.

The region of concentrations in this procedure may seem to be too narrow, however it can be broadened to analyse more concentrated or more dilute solutions than those giving minimum currents (Fig. 6). Although this can be done with any technique, in this case the morphology of the wave (*i.e.* the variation of the current in the maximum and at potentials more positive than those where the polarographic minimum appears) allows the concentration of the surfactant to be evaluated approximately.

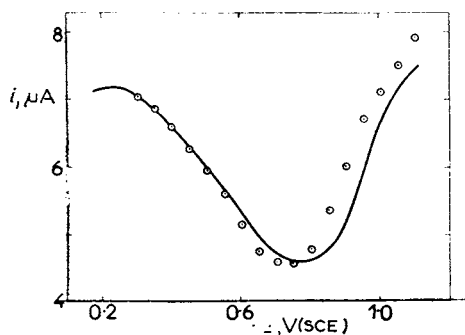


FIG. 5

Polarographic curve corresponding to concentration of SDS 0.6 mmol l^{-1} . Full line is experimental, points were calculated from Eq. (1) based on the values of Θ_2 from Fig. 4

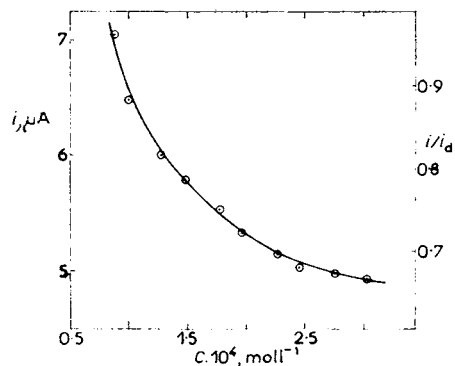


FIG. 6

Plot of the current at the polarographic minimum, i , and i/i_d against the concentration of SDS. Example of a calibration curve for determination of the surfactant concentration

Since the effect of the majority of surfactants on the polarograms of the system Bi(III)–HCl is similar to that of SDS, the treatment developed here can be extended to any of them with no other prerequisite than a similar calibration curve for these substances, thus providing a method by which any surfactant can readily be determined in aqueous solution.

In order to make the calibration curve independent of the experimental conditions, the ratio of the current at the minimum to the diffusion current, i/i_d ($i_d = 7.35 \mu\text{A}$ in the present work) is represented on the right ordinate in Fig. 6. The accuracy of the method corresponds to the polarographic quantitative analysis.

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