

Characterisation of streaming polarographic maxima

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Abstract. The observed polarographic maxima of oxygen, Pb^{2+} , Tl^+ , Ag^+ , UO_2^{2+} and 9,10-diphenyl anthracene anion were eliminated by using Triton X, Tweens and sulphonated aryl stearic acids. The maxima characteristics revealed that Ag^+ produced maxima of third kind, while organic anion displayed a mixed kind maxima. UO_2^{2+} and Tl^+ are characterised to yield maxima of second kind while oxygen and Pb^{2+} gave maxima of first kind.

Keywords. Surface active substance; zero charge; polarography; drop time.

1. Introduction

Bauer (1975) and subsequently Gupta (1978) clearly differentiated between various kinds of streaming maxima observed under different conditions. A variety of compounds are in use to suppress maxima. Tweens (polyoxyethylated surfactants), sulphonated aryl stearic acids (Malik and Jhamb 1972) and Triton X (alkyl phenoxy polyethoxy ethanols) (Kumar and Gilbert 1972), are amongst the newer compounds to be employed for this purpose. In this investigation, the role of the compounds belonging to these three series on the polarographic maxima of oxygen, simple and complex metal ions and an organic compound has been presented. The observed characteristics establish the kind of the maxima.

2. Experimental

2.1. Polarograms

Current voltage curves were recorded ($25 \pm 0.1^\circ$) with Cambridge pen recording polarograph. The capillary characteristics were $m = 1.84$ mg/s and $t = 3.52$ s in 0.1 M KCl at $h = 51.0$ cm of mercury reservoir. An external saturated calomel electrode with an agar bridge served as the reference electrode. An H-shaped cell was employed in all measurements. One compartment of the cell in which the agar bridge was immersed contained only supporting electrolyte. For each set of measurements 20.0 ml of the test solution was placed in the cell and

the surface active substance was added from the microburette (Metrohm E 457). Except in the case of the studies involving oxygen maxima, pure, dry nitrogen was bubbled for 10 min through the solution to deaerate it. During the course of measurement, nitrogen was allowed to flow over the surface of the solution.

2.2. Measurement of drop time

Drop time curves from 0.0 to -1.3 V vs SCE were measured using a manual polarograph LP 55 Heyrovsky model in conjunction with a Pye scalamp galvanometer. The time taken by 5 drops was determined for each applied potential at a constant height of mercury reservoir. Increments of the freshly prepared suppressors were added and the complete curve determined after each addition.

2.3. Reagents

Triton X-45, X-100, X-205 and X-405 (Rohm and Haas) were used without further purification. Tween 20 (polyoxyethylene sorbitan monolaurate), Tween 40 (polyoxyethylene sorbitan monopalmitate) and Tween 80 (polyoxyethylene sorbitan monooleate) were the products of Atlas Chemical Co. and were used as such. Sulphonated phenyl, tolyl and xylyl stearic acids (SPSA, STSA and SXSA) respectively were prepared by the method of Stirton *et al* (1940) and were recrystallised twice before use. The solutions were prepared in doubly distilled water. All other reagents were guaranteed chemicals.

3. Results and discussion

The numbers of depolariser-supporting electrolyte systems studied are summarised in table 1. Table 1 also represents the maximum suppression point of different suppressors for oxygen, Pb^{2+} , UO_2^{2+} , Tl^+ , Ag^+ and 9,10-diphenyl anthracene anion radical (stabilised in DMF) studied in various supporting electrolytes. The following observations are of interest :

- (i) A small amount of suppressor is needed for the systems 5 and 6, i.e. UO_2^{2+} (0.1 M HCl) and Tl^+ (0.1 M Na_2SO_4).
- (ii) Higher concentrations of the suppressor is required by the systems 7 and 8 to suppress the maxima.
- (iii) Systems 1 to 4 roughly average between the above two limits.

Subsequently, Triton X is generally made away with the least amount of other two series; while Triton X-100 is used up to the minimum amount amongst the Triton serie.

In a recent review, Gupta (1978, and references given therein) highlights the various distinguishable parameters that exist between different kinds of maxima. It was observed that Ag^+ in Na_2SO_4 (system 7) yields a small but effective maxima ($i_m/i_d = 2.1$) which is much more difficult to eliminate even by 20-fold excess of the recommendable limit of a suppressor. However, the maxima increase at first with the smaller addition of the SAS and recedes with much higher concentration of SAS. The electrocapillary maxima appear exactly at PZC (-0.50 V); these parameters depicts the maxima of third kind. The appearance of two armed maxima in the presence of larger concentrations of SAS away from PZC adds to

Table 1. MSP ($\times 10^4$ M) of various suppressors for different electroactive depolarisers in different electrolytes ($25 \pm 0.1^\circ$).

System	Depolarisers	Supporting electrolyte	Twcen-20	-40	-80	SPSA	STSA	SXSA	Triton X-45	X-100	X-205	X-405
1.	Oxygen	(0.01 M NaCl)	160.0	181.2	212.3	136.0	152.4	152.1	20.3	19.6	23.5	23.8
2.		(0.01 M KCl)	172.0	191.8	218.3	138.8	148.3	153.5	20.8	20.1	22.1	22.0
3.	1 mM Pb ²⁺	(0.1 M LiCl)	144.5	140.1	134.2	166.0	161.2	158.5	14.2	14.0	14.3	14.4
4.		(0.1 M KCl)	144.3	140.3	135.1	166.0	161.4	161.6	14.3	14.0	11.4	11.6
5.	2 mM UO ₂ ²⁺	(0.1 M HCl)	89.4	90.3	91.3	116.0	112.0	110.3	12.1	12.0	12.6	23.0
6.	1 mM Tl ⁺	(0.1 M Na ₂ SO ₄)	72.0	70.1	66.2	65.0	63.0	66.0	9.0	8.4	9.3	16.6
7.	1 mM Ag ⁺	(1 M Na ₂ SO ₄)	11800.0	..	11000.0	9100.0	9000.0	..	8600.0
8.	9,10-diphenyl anthracene anion (DMF)	(Buffer pH 7.0)	4140.0	4000.0	3810.0

Table 2. Characterisation of the maxima.

Shape and Position (V)	Systems (vide table 1)							
	1	2	3	4	5	6	7	8
i_{ml}/i_d	Sharp ≈ 0.51	Sharp ≈ 0.52	Very acute ≈ 0.31	Very acute ≈ 0.36	Round ≈ 0.58	Round ≈ 0.46	Round ≈ 0.50	Sharp ≈ 0.50
Maxima appears at :	21.7	20.1	9.4	13.6	5.8	5.4	2.1	40.1
Hanging drop	Yes	Yes	Yes	Yes	No	No	No	Yes
Rotating drop	No	No	No	No	Yes	Yes	No	No
Stirred solution	No	No	No	No	Yes	Yes	Yes	Yes
Mercury Pool	Dep.	Dep.	Dep.	Yes	No	No	No	Yes
Capillary Character	Indep.	Indep.	Indep.	Indep.	$x = 0.89,$ $y = 0.71,$ $z = 2.0 (25^\circ)$	$x = 1.40,$ $y = 0.23,$ $z = 1.0 (25^\circ)$
$m^2 r^2 c^2$	First positive	First positive	First Negative	First Negative	Second	Second	Third	Mixed

the confirmation of this kind of maxima. The maxima was not observed with hanging mercury drop electrode, thereby reassuring the third kind of maxima for the system Ag^+ in Na_2SO_4 .

9,10-diphenyl anthracene anion radical in DMF is another interesting system, where SPSA and Triton X 405 are the most effective suppressors though appreciably higher amount of suppressors are used up (less as compared to Ag^+). The ratio of i_m/i_d is high (40.1) which favours first positive kind but increase in i_m/i_d in the presence of small amount of suppressor and appearance at PZC indicates a third kind maxima. The maxima also appear at mercury pool and hanging drop electrode. These evidences indicate a mixed type of maxima of first and third kind.

The widely accepted explanation of maxima of third kind is due to Frumkin *et al* (1971). According to him unequal adsorption takes place at the surface followed by unequal surface tension on mercury/solution interface resulting in an erratic streaming. The stirring action and natural convections may enhance the surface activity at the mercury/solution resulting in unequal surface tension as observed by O'Brien and Dieken (1973) for the maxima of third kind but in the opinion of the present author the contribution due to these factors will be small and negligible.

The maxima of first positive kind is established beyond doubt for oxygen in 0.01 M NaCl as well as in 0.01 M KCl (vide table 2). The presence of unequal current density at the covered surface of the electrode (positive) results in non-uniform interfacial potentials, consequently, the difference in surface tension is produced. This phenomenon disturbs the growth of the drop and electrolysis past the drop surface indulges in streaming. Positive maxima are always acute, generally catalytic in behaviour and hence the i_m/i_d value is the highest of all other maxima. The maxima of first negative kind observed with Pb^{2+} in LiCl and KCl can be explained on similar grounds with the difference that the formation of torus further stabilises the streaming conditions in accordance with the observations of O'Brien and Dieken (1970).

Table 3. Effect of supporting electrolyte to depolariser ratio on the MSP ($\times 10^6$ M) of Pb^{2+} and Tl^+ .

Depolariser	Supporting electrolyte	Tween 20	SPSA	Triton X-100
1 mM Pb^{2+}	0.2 M KCl	111.6	2.4	1.8
	0.5 M KCl	94.2	1.9	1.2
	1.0 M KCl	62.2	1.3	1.0
	2.0 M KCl	10.7	1.0	1.0
1 mM Tl^+	0.2 M Na_2SO_4	62.9	60.0	25.4
	0.5 M Na_2SO_4	60.0	59.1	25.3
	0.8 M Na_2SO_4	59.5	58.2	25.3
	1.5 M Na_2SO_4	58.2	55.0	25.2

The maxima of second kind occur at both sides of the PZC and generally possess the i_m/i_a ratio much less than the positive kind and are higher than third kind. Its appearance is hump-like. UO_2^{2+} and Tl^+ gives properties clarifying a second kind of maxima. The explanation for this kind of maxima is probably the fast filling of the drop and naturally depends on the capillary dimension. Kovaienko *et al* (1969) framed several empirical equations to study the effect of capillary on the maxima of second kind. These equations fit well into the observed data with UO_2^{2+} and Tl^+ (vide table 2).

The amount of supporting electrolyte affects substantially the first kind of maxima but not the second kind (Gupta 1978). The studies in this respect have been undertaken with Pb^{2+} and Tl^+ in different amounts of supporting electrolyte and the results are shown in table 3. The observation clearly indicates that Pb^{2+} gives a maxima of first kind and Tl^+ of second kind.

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