TECHNICAL REPORT

STREAMING MAXIMA AT THE MERCURY / SOLUTION INTERFACE A CONCISE REVIEW

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The importance of polarography is being felt exceedingly more in recent years in pharmacology[1] and environmental conservation[2] due to its easier experimentation and quicker computation of results but the frequent appearances of maxima often complicates its utility for accurate analysis. Polarographic maxima is a difficult problem and the causes of its occurrence varies from more than one reason. Polarographic maxima other than catalytic[3] (or psuedocatalytic) is brought about by a complex behaviour of streaming past the mercury/solution interface by diffusion, which contributes to the changes in the electrical double layer around the drop. Ohsaka et al[4] explored adsorption effects of different Triton X (alkyl phenoxy polyethoxy ethanols) by measurements of differential capacity and instantaneous current at the drop. Similar studies were undertaken for poly vinyl pyrrolidones[5] and poly ethylene glycols[6] and confirmed the validity of the equation given by Koryta[7]. The measurements of maximum surface tension proved yet a better method for the study of oxygen maxima suppression in the presence of Triton X[8].

Three kinds of streaming maxima are generally encountered in polarographic analysis. A large variety of compounds of varied nature are in use to suppress maxima, but gelatin, Triton X-100, and methyl red are being employed universally. In recent years many more suppressors viz., Tweens (polyoxyethylated surfactants)[9], sulphonated aryl stearic acids[9], nonanioc acid[10], borneol, adamentols and adamantoic acids and 2-hydroxy adamantane[11], cyclohexanones[12], aromatic[13] and aliphatic amines[14] and sodium alkyl sulphates[15] have been reported for the suppression of maximas of simple and complex metal ions as well as of charged and uncharged organic molecules.

According to Bauer[16] the origin of streaming forces may take place from either of the following causes: (a) Nonuniform difference of potential at mercury/solution interface due to distribution of unequal current first kind); (b) Rapid filling of mercury drop (second kind); (c) Nonuniform adsorption (third kind).

The maxima of second and third kinds have yielded to simple explanation at this stage, though more work may prove otherwise, whereas the theory of the maximum of first kind is the most complicated. In Table I, the properties of all these types are summarised alongwith their possible prevention.

Maxima of first kind

The maximum of first kind is subdivided into two, positive and negative. The maximum of first kind is dependent upon the induced depolarisation effect after the initiation of the streaming; on alignment it gives rise to positive maxima, while hindrance causes negative maxima; in other words i_m/i_d would be expected to be higher in the case of positive first kind than the latter.

Interferometry results of O'Brien and Dieken[17] indicated that positive maximum is a down flow annulus with a mild upwelling interior below the equator of the drop and negative maximum flow is due to torroidal whirl surrounding the drop. Kambara et al[18] showed that the difference of surface tension may arise at the upper and lower end of the drop due to spontaneous streaming of mercury and electrolytic solution which in turn would cause local c.d. differences. These views were argumented by experimentation and later supported by Bauer[19] and advanced the reasons for much more acuteness of the negative kind than the positive one.

It is reported that cation of the alkali metals suppresses various maxima increasingly in order of $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$; despite lack of evidence for their adsorption from aqueous medium, however, the influence of the higher concentration of these ions to eliminate maxima is in favour of the theory[20]. The maxima of first kind do not occur in strong electrolyte

(HCl) but with one exception[21]. They also do not occur in the vigorously stirred solution[22], but do appear at hanging drop as well as in a mercury pool electrode[17].

A compatible description establishing the first order maxima is founded by considering unequal current distribution at the d.m.e. on a mathematical basis is due to Levich modified by Bauer[19], though yet not completely free from all objections.

Maxima of second kind

Second kind of maxima (generally round shape) may combine with first kind which sometimes complicates its evaluation further. Since these are the result of fast-filling of the drop it is obvious that it would depend on geometric dimension of the capillary viz., diameter, length etc., to this effect various empirical equations have been framed by Kovalenko et al[23] and naturally its validity is approximate. Kumar and Bauer[24] further investigated the capillary characterestics and found that in the absence of impurities, the current depends upon $m^x t^y c^z$ and varified for Cu^{2+} (25°) x=1.38, y=0.22 and z=1.0 while for Cd^{2+} (25°) x=1.24, y=0.22 and z=1.0. The current is a linear function of concentration and the temperature dependence of the current is also of the same magnitude as expected for diffusion current[25].

The hydrodynamic flow of mercury inside the drop causing upward streaming of Hg at the sides of the growing drop electrode is attributed to the second kind of maxima. The upward streaming of the solution around the d.m.e. is simultaneously effected by the presence of depolariser, thereby accounting the rate of streaming of the solution[26]. It is worth to point out here that any attempt to slow the rate of filling of drop would appreciably reduce the maxima. If this is not possible a very small amount of surface active agents capable of forming a thin layer around the mercury would eliminate the maxima completely.

Major differences are reported by the use of three-electrode system as compared with the results obtained by employing two-electrode circuit, but the studies in this field are restricted[27]. A study of Table I would reveal that it is still impossible to differentiate clearly between first and second kind maxima; a detailed study by Holt and Bauer[28] recommends that current-time behaviour enables the clearest distinction between them.

Maxima of third kind

The streaming maxima of third kind on polarographic curves are caused by the tangential motion of SAS by the adsorption on mercury drop. Evidence in support of adsorption was given by observing the reduction of metal ions in the presence of camphor. The $E_{\frac{1}{2}}$ values of Cu^{2+}, Cd^{2+} and Bi^{3+} in different supporting electrolytes were found to be very near the potential of camphor, also closer to the point of zero charge (PZC), at which maximum adsorption occurs[29]. This kind of maximum is generally two-armed in latter stages but always appears at PZC. Frumkin et al[30] studied this kind of maxima in 1M Na_2SO_4 for $AgNO_3$ in the presence of various concentrations of camphor, borneol and 1-adamantol. In the presence of these surfactants at concentration 1.5×10^{-5}M in solution of 10^{-3} N $AgNO_3$ + 1M Na_2SO_4, an increase in i_m was observed up to a value markedly higher than i_d at PZC. This increase is found to depend on the degree of surface coverage 'θ' (=0.47). The maximum disappears in the region of PZC after further addition of surfactants and the waves (mostly two) appears only at those potential values where 'θ' changes from $1\rightarrow0$. A similar effect was observed in the case of nonanioc acid at the mercury surface in the presence of $CdSO_4$ and $MgSO_4$[31].

An additional remark must be made about the impurities to which this kind of maxima is extremely sensitive; therefore, the purification of solutions must be given utmost attention before drawing any useful conclusion[32].

Gupta et al [33–34] studied the polarographic reduction behaviour of various solochrome mordant dyes in different buffers and at different concentrations of the depolarisable dye. Solochrome yellow 2 GS produced an intense maxima at and beyond a concentration of 5×10^{-4} M and can be eliminated by Triton X. Recently it was established that the maxima was of the first kind positive[35].

In a detail study on expolaring the behaviour of suppressors, Gupta[36] established that several factors viz., viscosity activity coefficients, temperature variations, conductance etc. play an important role on the characteristics of a maxima and holds the view that unless these parameters are given their due consideration no theory on maxima can be founded on firm grounds.

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TABLE I : Characteristics of various maximas

		FIRST		SECOND	THIRD
		Positive	Negative		
1.	Characterised by	both by	Heyrovsky[37]	Kryukova[38]	Frumkin[30]
2.	Shape	acute	most acute	rounded	Previously round followed by two-armed.
3.	i_m/i_d	10–50	5-20	6	3
4.	Position	ca 0.5v	ca 0.25v	0.5v	PZC
5.	Effect of impurities	both	sensitive	—	highly sensitive
6.	Occurs at :				
	Hanging Hg drop	both yes		No	—
	rotating Hg drop	both yes		yes	No
	solid electrode	both No		—	yes
	stirred solution	both No		yes	yes
	Hg pool	both yes		—	yes
7.	Effect of :				
	Supporting electrolyte	both dep.		dep.	ind.
	Electroactive species	both dep.		dep	ind.
	Suppressors	both dep.		dep.	dep.
8.	Capillary character	both varies		dep. substantially	ind.
9.	Cause	non-uniform current distribution		fast filling of Hg drop	non-uniform adsorption.
10.	Interferometry results	no movement below drop.	Below drop, mild changes are observed.	mild torus, strong movement below drop.	
11	Prevention	1. both suppressed by medium concentration of suppressors.		1. low m & high t. 2. inclined capillary	1. removal of org. impurities. 2. suppressors (1) or (2) adamantol
		2. high conc. of supporting electrolyte.		3. low conc. of gelatin, ionic & non-ionic detergents.	borneol, camphor, nonanioc acid.

REFERENCES

1. F. Billand, M.F. Hutin, P. Bourret and D. Burnnel, Ann. Biol. Clin (Paris), 35 (1977) 51.
2. K. Gorzka, A. Jozwait and A. Socha, Metody Fizyko-chem. Oczyszczania wod Sciekow, 1 (1976) 44.
3. T. Miazgowska and E. Weronski, Rocz. Chem., 45 (5) (1971) 877.
4. T. Ohsaka, H. Yamamoto and T. Yoshida, Bull. Chem. Soc. (Japan), 46 (1973) 1320.
5. T. Yoshida, T. Ohsaka and S. Tanaka, Bull. Chem. Soc. (Japan), 45 (1972) 326.
6. T. Yoshida, T. Oshaka and M. Suzuki, Bull. Chem. Soc. (Japan), 45 (1972) 3245.
7. J. Koryta, Coll. Czech. Chem. Comm., 18 (1953) 206.
8. R.G. Barradas and F.M. Kimmerle, J. Electroanal. Chem., 11 (1966) 163.
9. W.U. Malik and O.P. Jhamb, J. Amer. Oil Chem Soc., 49 (1972) 170.
10. F.V. Stenina, A.N. Frumkin, I.V. Osipov and N.V. Fedorovich, Elektrokhimiya, 12 (1976) 1149.
11. E.V. Stenina, N.V. Fedorovich and G.N. Petukhova, Elektrokhimiya, 12 (1976) 1824.
12. S.R. Vishvanath, S. Sathyanareyana, S.K. Rangarajan, J. Electroanal. Chem. Interfac. Electrochem. 63 (1976) 377.
13. L. Narebska, ibid., 49 (1974) 321.
14. R. Shivakumar, C.R. Dharmaraja, T.K. Venkatachalam and J. Sunderarajan, J. Electrochem. Soc. (India), 25 (1976) 73.
15. V. Kumar and T.W. Gilbert, J. Electroanal. Chem. Interfac. Electrochem., 40 (1972) 419.
16. H.H. Bauer, Electrochem. Acta., 18 (1973) 355.
17. R N. O'Brien and F.P. Dieken, Can. J. Chem., 48 (1970) 2651.
18. T. Kambara, J. Kitamura and K. Ohzeki, Denki Kagaku Oyobi Kogyo Butsuri Kagaku, 39 (1971) 677.
19. H.H. Bauer, Electrochem. Acta., 18 (1973) 427.
20. H.H. Bauer and M. Goebes, J. Electroanal. Chem. Interfac. Electrochem., 49 (1974) 313 and 452.
21. L. Meites, 'Polarographic Techniques' Second ediction, (1952) p. 305, Inter Science Publisher, New York.
22. S. Iofa and A. Frumkin, Compt. Rend. Acad. Sci. USSR, 20 (1938) 293.
23. P.N. Kovalenko, N.A. Lektorskaya and I.L. Genov, Izv. Vyssh Ucheb Zaved., Khim Khim Tekhnol., 12 (1969) 889.
24. A. Kumar and H.H. Bauer., J. Electroanal. Chem. Interfac Electro Chem., 45 (1973) 187.
25. S. Lal and H.H. Bauer, Anal. Lett., 9 (1976) 13.
26. S. Lal, A. Kumar and H H. Bauer, J. Electroanal. Chem. Interfac. Electrochem., 42 (1973) 423.
27. F.M. Hawkridge, T.W. Holt and H.H. Bauer, Anal. Chim. Acta, 58 (1972) 203.
28. T.W. Holt and H.H. Bauer, US Clearinghouse Fed. Sci. Tech. Inform. A.D. 1970, No 715009, 47 pp.
29. L.S. Zagainova and A.V. Kuz'micheva, Vop. Khim. Khim. Tekhnol., 28 (1973) 88.
30. A.N. Frumkin, E.V. Stenina, N.V. Nikolaeva-Fedorovich, G.N. Petukhova, V.A. Yusupova and E.A. Shokova, Dokl. Akad. Nauk SSSR., 201 (1971) 1407.
31. E.V. Stenina, A.N. Frumkin, I.V. Osipov, N.V. Fedorovich, Elektrokhimiya, 12 (1976) 1149.
32. E.V. Stenina, N.V. Fedorovich and G.N. Petukhova, Elektrokhimiya, 12 (1976) 1824.
33. P.N. Gupta, C.N. Kachru and S.A. Bhat, J. Electrochem. Soc. (Japan) 46 (1978) 212.
34. P.N. Gupta, and W.U. Malik, J. Electroanal. Chem. Interfac. Electrochem., 54 (1974) 417.
35. P.N. Gupta, S. Ahmad and S.A. Bhat Z. Physik. Chem... in press.
36. P.N. Gupta, Ph.D. Thesis of J & K University, 1968, A.K. Bhattacharaya, J. Electrochem. Science and Tech., 2 (1967) 12., Proc. Symp. Electrode. Process. Jodhpur, 1966 Pub. (1968) 131., Indian J. App. Chem., 32 (1969) 17, 296-, 33 (1970) 219.
37. J. Heyrovsky, Actualit'es Scientifiques et. indus., 90 (1934) Paris.
38. T.A. Kryukova, Zavodskaya Lab., 9 (1940) 691., 14 (1948) 511.