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Polarographic Reduction of Sulfonamoyl Azopyrazoles in Nonionic and Cationic Surfactant Media: Double Layer, Micellar Hydration, and pH-Dependent H^+, e^-, e^-, H^+ Mechanisms at the DME

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Abstract

The polarographic reduction of 1-(carboxymethyl)trimethylammoniumchloride-3-aminophenyl-5-methyl-4-(4'-sulphonamoyl)azopyrazoles was studied in Britton-Robinson buffers with Tween-20 and CTAC surfactants. At pH 4.7, four derivatives showed well-defined waves: guanylsulphonamoyl ($E_{1/2}$ = -0.70 V), dimethylpyrimidinyl (-0.72 V), methoxazolylsulphonamoyl (-0.80 V), thiazolylsulphonoyl (-0.84 V). Surfactants adsorb on mercury, increasing double layer thickness and decreasing dielectric constant, reducing diffusion current (_i_d_) and heterogeneous rate constant (k°_f,h).

With CTAC (0→0.8%), _i_d_ decreased 3.2→1.0 µA and $-E_{1/2}$ increased 0.90→1.14 V, marking CMC and IHP saturation. Tween-20 ($1.0\times10^{-2}\rightarrow10.0\times10^{-2}$ M) decreased αn_a (0.45→0.28) and k°_f,h ($2.4\times10^{-4}\rightarrow3.0\times10^{-13}$ cm s^{-1}), indicating extreme irreversibility. At low pH, both surfactants shift $E_{1/2}$ negative; at mid-pH, Tween-20 catalyzes protonation more than CTAC. Substituent hydrophobicity controls micellar partitioning: thiazolyl > methoxazolyl > dimethylpyrimidinyl > guanyl.

1. Introduction

Electrical double layer at DME is modified by adsorption of surface active substances, which changes capacitance and electron transfer rates. Adsorption is maximum at Em near electrocapillary zero Ez, where streaming causes first kind maxima: i proportional to t^(1/3), i_max = kC^alpha (alpha = 1.6–1.8), optimum at k_opt = 1.5C, and about 100 mV hysteresis.

Surfactants suppress maxima by adsorption and immobilization of interface:

C = (2/(V*a)) * ((h1 - h)/h) (monomer)

C = (k/(V*a)) * (i/sqrt(h)) (micellar)

Above CMC, micelles have hydrophobic core and polar surface. They are important in biochemistry for lipid transport and as models of membrane regions. In polarography, they solubilize insoluble compounds, but adsorption changes phi2, partitioning and accessibility.

Compounds studied: 1-(carboxymethyl)trimethylammonium chloride-3-aminophenyl-5-methyl-4-(R) azopyrazole,

where R = 4'-guanylsulphonamoyl (1), 4'-(4",6"-dimethylpyrimidinylsulphonamoyl) (2), 4'-methoxazolylsulphonamoyl (3), 4'-thiazolylsulphonoyl (4).

These compounds are surface active and show maxima in buffer alone.

2. Experimental

Britton-Robinson buffers pH 2.67–4.7 + 1.0 M KCl. Surfactants: Tween-20 and CTAC, $0.1–10.0\times10^{-2}$ M or 0.1–2.0% v/v. Azopyrazoles 2.0×10^{-4} M or 1.0×10^{-3} M in DMF.

Solutions: 2.0 mL stock + 1.0 mL 1.0 M KCl + 7.0 mL buffer + surfactant, N_2 deaerated 10 min. DME: _m_ = 2.15 mg s^{-1}, _t_ = 3.2 s, 25°C, E vs SCE. Electrocapillary curves by drop-time method. αn_a and k°_f,h by Meites-Israel method.

3. Results and Discussion

3.1 Polarograms and Wave Morphology,

Fig.1 at pH 4.7 shows single, diffusion-controlled waves for (1)–(4) with $E_{1/2}$ = -0.70, -0.72, -0.80, -0.84 V. Current scale 0.30 µA. Wave heights follow _i_d_(4) > _i_d_(3) > _i_d_(2) > _i_d_(1),

reflecting substituent hydrophobicity: thiazolyl > methoxazolyl > dimethylpyrimidinyl > guanyl. More hydrophobic substituents partition deeper into micelles, lowering _D_ and _i_d_. $E_{1/2}$ becomes more negative with electron-withdrawing sulphonamoyl substituents, consistent with LUMO stabilization.

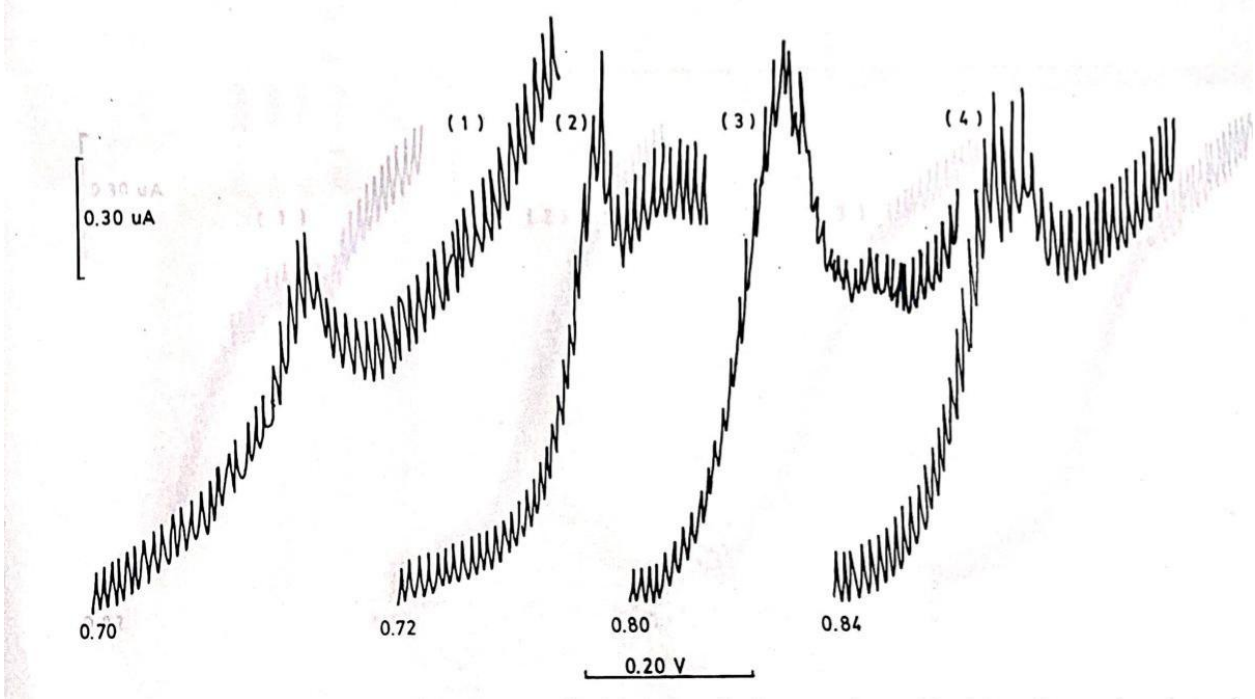


Fig. 1. Polarograms of
1-(carboxymethyl)trimethylammonium chloride-3-aminophenyl-5-methyl-4-(1) [4′-guanidylsulphonamoyl];
(2) [4′-(4″,6″-dimethylpyrimidinyl)sulphonamoyl];
(3) [4′-methoxazolylsulphonamoyl];
(4) [4′-thiazolylsulphonamoyl] azopyrazole at pH 4.7.

Fig.2 for the 4'-(4",6"-pyrimidinyl) derivative shows that increasing CTAC shifts $-E_{1/2}$ from 0.82 V to 0.90 V across waves (1)→(4) and decreases wave height, confirming suppression and negative $E_{1/2}$ shift with adsorption.

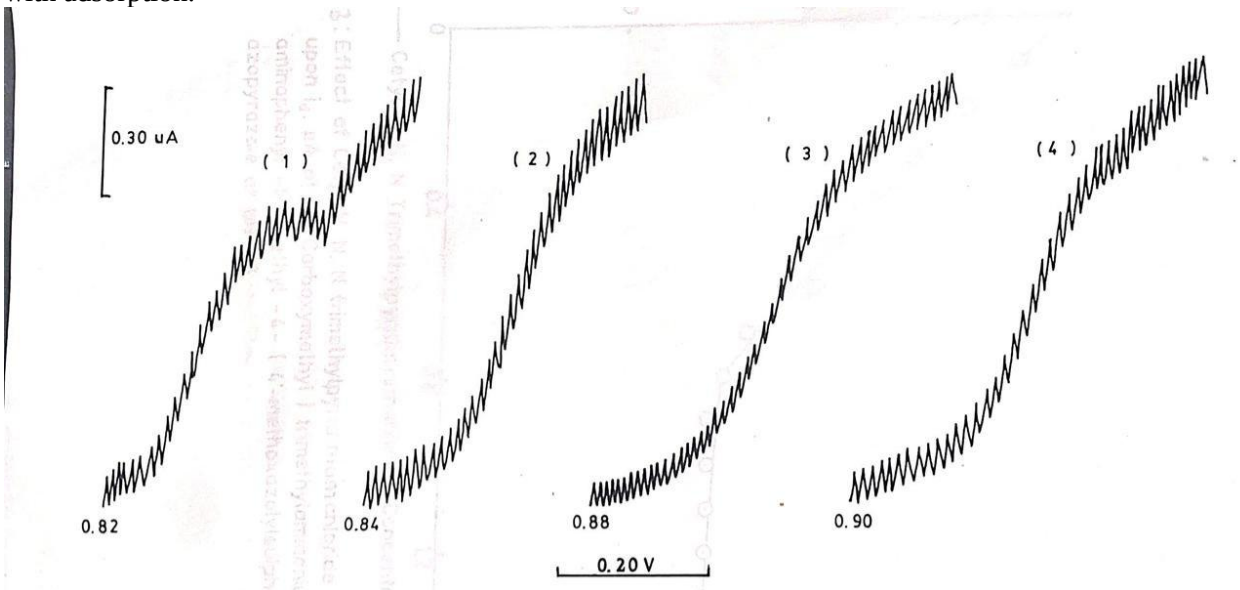


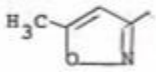
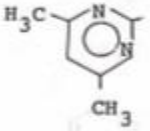
Fig. 2. Effect of increasing concentration of surfactant CTAC on 1-(carboxymethyl) trimethylammonium chloride-3-aminophenyl-5-methyl-4-(4′,6′-pyrimidinylsulphonamoyl) azopyrazole.

3.2 Electrocapillary and Dielectric Evidence

Both Tween-20 and CTAC adsorb on the negatively charged electrode. Electrocapillary maxima shift positive and show a downward dip, confirming adsorption. Adsorption decreases double layer capacity because it separates the double layer and lowers dielectric constant between electrode and OHP. Increased thickness thus decreases _i_d_, as observed in table (1,2). It also slows electron uptake by species (VII), lowering k°_f,h and αn_a, increasing irreversibility.[3]

Table 1

Values of -E1/2 (V) and i_d (uA) for 1-(carboxymethyl)trimethylammonium chloride-3-amino-phenyl-5-methyl-5-(4'-sulphonamoyl)azopyrazole in Tween-20 at different pH ,Concentration: 2.0 x 10^-4 M

S. No.	R	pH 2.7		pH 3.6		pH 4.7	
		$-E_{1/2}$, V	i_d, µA	$-E_{1/2}$, V	i_d, µA	$-E_{1/2}$, V	i_d, µA
1.		0.98	2.02	1.02	2.32	1.12	2.60
2.		0.94	2.25	1.00	2.30	1.10	2.62
3.		0.98	2.80	1.00	2.86	1.04	3.02

3.3 CTAC Concentration Effect

Fig.3 for (3) 4'-methoxazolyl at pH 3.6 shows _i_d_ decreases linearly from 3.2 µA at 0% to 1.0 µA at 0.8% CTAC, then remains constant to 1.4%. Simultaneously, $-E_{1/2}$ increases from 0.90 V to 1.14 V then plateaus. Curves (1) and (2) show similar $-E_{1/2}$ increases to constant values.

This matches Table-2: for (3), 0.1% → 0.7% CTAC, $-E_{1/2}$ = 1.02 → 1.14 V, _i_d_ = 3.40 → 1.80 µA, then constant. Shift = -120 mV; _i_d_ drop = 47.1%. For (2), 0.1% → 0.8% CTAC, $-E_{1/2}$ = 0.98 → 1.16 V, _i_d_ = 2.40 → 1.80 µA. Shift = -180 mV; _i_d_ drop = 25.0%.

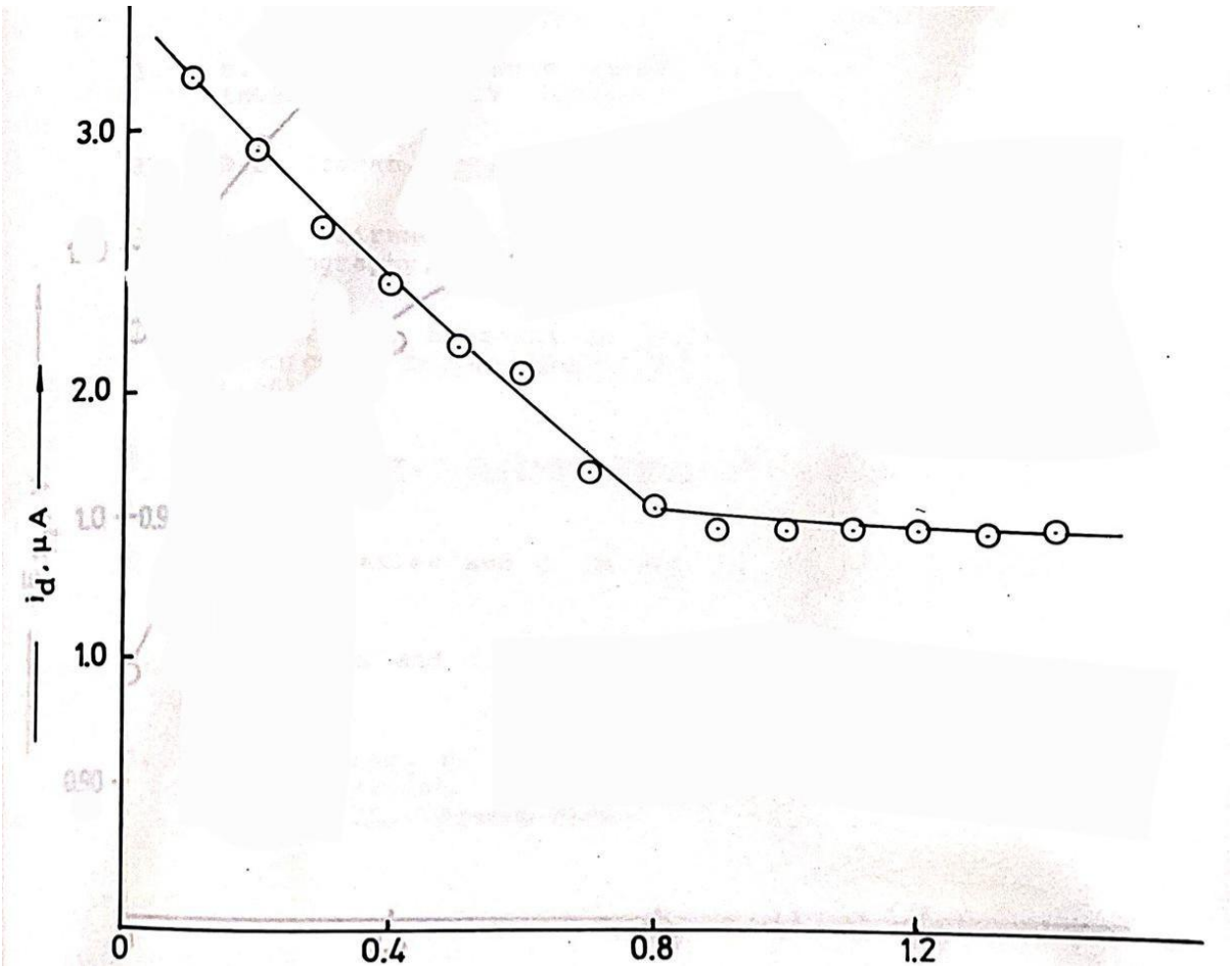


Fig. 3 - Effect of CTAC concentration (%) upon i_a (μA) of 1-(carboxymethyl)trimethylammonium chloride-3-aminophenyl-5-methyl-4-(4′-methoxazolylsulphonamoyl

The breakpoint at 0.7–0.8% CTAC corresponds to CMC (~6×10^{-4} M). Below CMC, monomers adsorb and gradually increase film thickness, giving linear _i_d_ decrease and $E_{1/2}$ shift. Above CMC, IHP is saturated and micelles dominate bulk; further CTAC does not change IHP composition, so $E_{1/2}$ and _i_d_ are constant. The large _i_d_ drop for (3), 47.1%, indicates strong interaction of cationic micelle with methoxazolyl derivative.

3.4 Tween-20 Concentration and Kinetic Effects

Table-2 at pH 2.67: for (2), 0.1% → 0.6% Tween-20, $-E_{1/2}$ = 0.98 → 1.16 V, _i_d_ = 2.02 → 1.65 μA, then constant. Shift = -180 mV; _i_d_ drop = 18.3%. For (1): 0.94 → 1.10 V, _i_d_ = 2.25 → 1.60 μA. Shift = -1

Table 2

Polarographic characteristics for 1-(carboxymethyl) trimethylammonium chloride–3-aminophenyl-5-methyl-4-(4′-sulphonamoyl)azopyrazole at different concentrations of Tween-20 at pH 2.67.

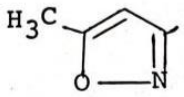
S. No.	R	Conc. %	$-E_{\frac{1}{2}}$, V	i_d, μA
1.		0.1	0.98	2.02
		0.2	1.08	1.87
		0.3	1.10	1.80
		0.4	1.12	1.72
		0.5	1.14	1.70
		0.6	1.16	1.65
		0.7	1.16	1.65
		0.8	1.16	1.65
		0.9	1.16	1.65
		1.0	1.16	1.65
2.		0.1	0.94	2.25
		0.2	0.96	2.15
		0.3	1.00	1.97
		0.4	1.02	1.92
		0.5	1.04	1.87
		0.6	1.06	1.68
		0.7	1.10	1.60
		0.8	1.10	1.60
		0.9	1.10	1.60
		1.0	1.10	1.60

Table-3 at pH 4.7 for (3) gives kinetic data: Tween-20 1.0×10^{-2} M → 10.0×10^{-2} M, $\alpha n_a = 0.45 \rightarrow 0.28$, k°_f,h = $2.4\times10^{-4} \rightarrow 3.0\times10^{-13}$ cm s^{-1}. Thus αn_a decreases 38% and k°_f,h decreases 9 orders of magnitude over one decade of concentration. This extreme irreversibility arises because the adsorbed polyoxyethylene film increases distance of closest approach and lowers ε, making electron tunneling nearly impossible. The constant _i_d_ region corresponds to saturation of this film at CMC.

Table 3 - Effect of Tween-20 (0.1%) on the kinetic parameters of 1-(carboxymethyl)trimethylammonium chloride-3-aminophenyl-5-methyl-4-(4′-methoxazolyl sulphonamoyl)azopyrazole at pH 4.7

Tween-20 (M/L)	αn	$K^{\circ}_{f,h}$ (cm/sec)
$1.0X10^{-2}$	0.45	$2.4X10^{-4}$
$2.0X10^{-2}$	0.44	$3.1X10^{-5}$
$3.0X10^{-2}$	0.42	$1.2X10^{-6}$
$4.0X10^{-2}$	0.40	$2.2X10^{-7}$
$5.0X10^{-2}$	0.38	$1.6X10^{-8}$
$6.0X10^{-2}$	0.36	$4.0X10^{-9}$
$7.0X10^{-2}$	0.35	$1.6X10^{-1}$
$8.0X10^{-2}$	0.32	$2.6X10^{-1}$
$9.0X10^{-2}$	0.30	$2.5X10^{-}$
$10.0X10^{-2}$	0.28	$3.0X10^{-}$

3.5 pH Effects,
Table-1, 2.0×10^{-4} M Tween-20: for (2), pH 2.7→3.6→4.7, $-E_{1/2}$ = 0.98→1.02→1.12 V; _i_d_ = 2.02→2.32→2.60 µA. For (1): 0.94→1.00→1.10 V; _i_d_ = 2.25→2.30→2.62 µA. For (4): 0.98→1.00→1.04 V; _i_d_ = 2.80→2.86→3.02 µA.

With increasing pH, $E_{1/2}$ becomes more negative and _i_d_ increases because H^+ availability decreases, requiring more negative potential, while micellar binding weakens, increasing free depolarizer and _D_. _i_d_ for (3) in CTAC is nearly constant with pH, showing strong binding even at pH 4.7.

3.6 Nonionic vs Cationic: Hydration and Catalysis

"Comparatively more positive shift in $E_{1/2}$ in non-ionic surfactant may be attributed to the hydration… In the micellar solution of Tween-20 the polyoxyethylene chain have the configuration of expanding spiral (a cone shape)… provides space for trapping of water molecules… hydrogen bond formation between water molecules and the ether oxygen… interaction of ether oxygen… with polarized $-N^+=N^-$– becomes more facile than in cationics… The catalytic effect will, therefore, be lesser in the case of cationic surfactant."

At pH 4.6–7.0, Tween-20 gave +80 mV shift, CTAC +40 mV. At pH 2.67–3.6, both give negative shifts because H^+ is not limiting. Thus the "more positive shift in non-ionics" is pH-dependent and reflects H-bonded proton relay.

3.7 Mechanistic Pathways

Surfactant micelles do not diffuse intact to the OHP; the surfactant-depolarizer complex reaches the IHP.

Tween-20 mechanism:

CTAC mechanism:

1. Ph-N=N-R + H+ -> (II) -> e- -> (III) Ph-N•-NH-R
2. (III) + CTAC -> complex (IV)
3. (IV) diffuses to IHP, + e- -> (V), + H+ -> (VI) + CTAC (released).

"In this mechanism free radical (III) is forming a complex with the surfactant, this complex may diffuse to the inner part of the double layer and get reduced to (VI) after the uptake of an electron and a proton, finally releasing the surfactant as such."

Tween-20 mechanism:

1. Ph-N=N-R <-> Ph-N(+)-N(-)-R
2. Hydrated PEG cone H-bond with IHP water, gives H+:
   Ph-N(+)-NH-R (XII)
3. (XII) + 2e- + H+ -> Ph-NH-NH-R (XIV)

At pH 2.67, step 2 is fast; step 3 is slow due to film, giving negative $E_{1/2}$ shift and very low k°_f,h as in table 3

3.8 Substituent Effects

_i_d_ order in all tables and Fig.1: thiazolyl (4) > methoxazolyl (3) > dimethylpyrimidinyl (2) > guanyl (1), correlating with increasing hydrophobicity and micellar binding. $E_{1/2}$ order is reverse at low surfactant but converges at high surfactant where surface saturation occurs.

4. Conclusion

Tween-20 and CTAC adsorb on the negatively charged DME, shifting electrocapillary maxima positive and decreasing interfacial tension. Adsorption lowers dielectric constant and increases double layer thickness, decreasing _i_d_ and increasing irreversibility.

CTAC at pH 3.6, _i_d_ decreases linearly to 0.8% then plateaus, while $-E_{1/2}$ increases to 1.14–1.16 V then plateaus, marking CMC and IHP saturation. Tables-1,3 show similar behavior for Tween-20. Table-5 proves extreme irreversibility: $\alpha n_a = 0.45 \rightarrow 0.28$ and k°_f,h = $2.4\times10^{-4} \rightarrow 3.0\times10^{-13}$ cm s^{-1} for (3) in Tween-20, $1.0\times10^{-2} \rightarrow 10.0\times10^{-2}$ M.

At fixed surfactant, increasing pH from 2.7→4.7 makes $E_{1/2}$ more negative and _i_d_ larger, because proton availability decreases and micellar binding weakens. Nonionic Tween-20 gives a more positive $E_{1/2}$ shift than CTAC at mid-pH due to hydration of its cone-shaped polyoxyethylene chain that H-bonds to IHP water and catalyzes protonation of $-N^{+}=N^{-}-$. At low pH, blocking dominates and both give negative shifts. Cationics give less catalytic effect because the positive charge is fully available for electrostatic interaction.

The electroactive species is a surfactant-depolarizer complex: with CTAC, radical (III)→(IV)→(VI); with Tween-20, H-bonded water gives (XII)→(XIV) via H^{+}, e^{-}, e^{-}, H^{+}. Anionic SLS has minimal effect due to hydration. These results unify Frumkin adsorption, empirical suppression, and micellar electrochemistry for membrane-like electron transfer and provide quantitative kinetic criteria for surfactant selection in electroanalysis of azopyrazoles.[2][3][4][8]

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