EFFECT OF QUINOLONES ON POLAROGRAPHIC MAXIMA SUPPRESSION

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A Study using substituted Vinyl Quinolones on the Polarographic maxima proved the efficiency of these quinolone derivatives to eliminate the maxima. In most of the systems, it showed a remarkable activity It has been found that along with adsorption process, the structure of the quinolones also played a vital role in deciding their activity. It was evident that they were active over a wide range of potentials. The mechanism of adsorption and the activity are correlated in this communication.

It is well known that in polarographic works, maxima elimination has to be effected. Many workers[1—13] have suggested several compounds for this. But there appears meagre data on nitrogen containing compounds especially vinyl quinolones. It was thought that a study using the above compounds may throw some more light both on the adsorption phenomena and the structural effects.

EXPERIMENTAL

The quinolones were synthesised according to the procedure adopted by Shanmugam et al [14—18] using ortho-Amino carbonyl compounds and 3-Butenoyl Chloride The n.m r., i r. and mass spectra of these compounds were taken and their structures were confirmed. Stock solutions of 10^{-3}M of these quinolones were prepared using double distilled MeOH. Three indifferent electrolytes were chosen, namely KCl, NH_4Cl and tetraethyl ammonium iodide, each of 0.04M, 0.025M and 0.02M respectively. The studies were conducted for three pH ranges using acetic acid (0.2M) and Sodium Acetate (0.2M), as well as NaOH (0.4M . The pH values obtained were 3.8, 6.8 and 11—12 respectively. For Ni and Pb maximum studies, $NiSO_4$(10^{-3}M). Pb $NO_3)_2$(10^{-3}M) were used. All the p larograms were taken in a Sargent-Welch automatic Polarograph having the capillary with drop time 10 sec. A saturated calomel served as the reference electrode For oxygen maximum studies oxygen gas was bubbled from a cylinder. To confirm that methanol does not interfere in the study, trials were carried out using methanol alone and it showed no activity and retained the maximum. The current sensitivity were set at 0.150 μA/mm, 0.030 μA/mm and 0.060 μA/mm respectively for Oxygen, Lead and Nickel systems. The maxima were produced as per the usual methods reported earlier[19—20].

RESULTS AND DISCUSSIONS

Table I gives the current values observed for oxygen maximum in different supporting electrolytes and for three pH ranges in presence and absence of substituted quinolones. Examination of the values indicate that all the quinolones has brought down the maxima current value to zero. Since the oxygen maximum appears on the positive side of the ECM, the quinolones are thought to be adsorbed on the positively charged mercury surface by coulombic force of attraction. This is understandable because of the presence of electrons on the nitrogen, oxygen and in the vinyl group. It is also clear that the substituents whether methyl, methoxy or methylenedioxy had no appreciable effect during elimination of maxima. Hence at this stage it is difficult to predict which substituent had marked effect. In acid medium (pH 3.8) we cannot expect the coulombic force of attraction to exist in a greater extent since the quinolones may get protonated in the medium.

If this is the case then the vinyl group may play a predominent role in the adsorption process. In basic medium (pH 11 12) most of them had a remarkable activity indicating the fact that the adsorptive character of quinolones had not been affected by a change in the pH of the medium. These facts are mainly confined to oxygen maximum when KCl was used in the system. It is also probable that surface area of these compounds and geometry plays a role during adsorption as evidenced from earlier

TABLE—I **Current values in μA observed for oxygen maximum.** Bulk conc. of quinolones 10^{-3}M

SUPPORTING ELECTROLYTE																		
	KCl				TEAI						NH_4Cl							
Medium	N		A		B		N		A		B		N		A		B	
Vol, ml.	0	5	0	5	0	5	0	5	0	5	0	5	0	5	0	5	0	5
VQ	13.65	0	13.20	0	4.05	0	10.95	0	10.80	0	7.35	0	No	Max.	14.1	0	No.	Max.
MVQ	14.70	0	21.45	0	14.70	0	10.45	0	10.50	0	7.30	0	,,	,,	15.2	0	,,	,,
MMVQ	13.35	0	13.65	0	13.65	0	9.75	0	10.35	0	7.20	0	,,	,,	16.5	0	,,	,,
MDVQ	13.95	0	14.70	0	4.80	0	10.35	0	10.80	0	8.55	0	,,	,,	15.45	0	,,	,,

NOTE : For all the Tables N represents Neutral medium ; A represents Acid medium and B represents Basic medium

VQ : 3 – Vinyl – 2 – Quinolone; MVQ : 4 Methyl —3—Vinyl —2—Quinolone;

MMVQ : 7—Methoxy —4—Methyl —3—Vinyl —2 – Quinolone;

MDVQ : 6,7 – Methylenedioxy —3—Vinyl —2 – Quinolone.

work[21]. When tetraethylammonium iodide was used, the current values for maxima were shifted to lower regions. But all the quinolones retained their activity. Hence both a change in the pH and the above two electrolytes had not caused much variation in the activities. To probe further NH_4Cl was used and it was surprising that we could not produce the maxima both in neutral and basic media, even in the absence of quinolones. This proves that a change in the supporting electrolyte do cause some effect contrary to the previous electrolyte used. The non-occurrence of maximum in basic medium can be accounted by considering the explanation afforded by Millner[22]. It can also be understood through the papers by Raymon[23].

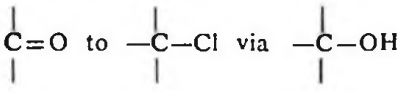
In order to confirm the activity of these compounds in a different environmental conditions, lead maximum studies were undertaken (Table II).

TABLE—II **Current values in μA observed for Lead Maximum.** Bulk conc of quinolone 10^{-3}M

Ref. Table I

SUPPORTING ELECTROLYTE																	
	KCl					TEAI						NH_4Cl					
Medium	N			A		N			A			N			A		
Vol, ml,	0	5	10	0	5	0	5	10	0	5		0	5	10	0	5	
VQ	0.72	0.57	0.96	2.73	0	0.75	0.24	0	1.53	0.66		0.90	0.45	0	4.05	0	
MVQ	2.61	0	.	2.10	0	0.45	0.42	2.52 (Double Max.)	1.74	0		0.87	0.75	0.54	3.45	0	
MMVQ	1.17	1.02	1.14	3.66	0	1.41	2.46	2.54 (Double Max)	3.78	0		1 83	1.23	0.57	4.25	0	
MDVQ	1.02	0	.	2.10	0	1.65	0	.	1.59	0		0.27	0.21	0	4.59	0	

In KCl supporting electrolyte system it is evident that 3—vinyl 2—quinolone and 7—methoxy —4methyl —3—vinyl 2—quinolone did not show much activity whereas 4—methyl 3—vinyl 2—quinolone and 6, 7 methylenedioxy, 3—vinyl 2—quinolone shows greater activity in neutral medium. It is known that Pb maximum occurs at a place which is neither +ve or —ve with respect to ECM and at this potential the charge on the Hg drop is almost zero. Hence at a different potential the adsorptive character for these compounds are different. In acid medium too, they retained their activity. The +ve species suggested earlier for quinolones in acid medium may get adsorbed on the Hg surface which is almost having a zero charge. How this type of adsorption is possible can be explained by the work of Raymon[23]. The existence of quinolones in the protonated form is supported by the fact that Shanmugam et al[15] converted the



In the case of tetraethyl ammonium iodide when used in these systems for neutral medium all the quinolones retained their activity, indicating again the effect of change in supporting electrolyte has some influence on their behaviour. In acid medium for the same supporting electrolyte except 3—vinyl 2—quinolone, others were found to be active. In the case of NH_4Cl system in neutral medium, most of them did not have much activity at lower amounts indicating that they are behaving entirely different when the environment is changed. This observation was comparable with the result of earlier work conducted with thiourea derivatives[24]. Since the experiments were conducted on the +ve side of ECM, it was thought that a study on —ve side is also essential to ascertain the activities shown by these compounds. For this purpose Ni maximum was selected. Table III gives the current values observed for Ni maximum in two pH values and for two supporting electrolytes. It was not possible to produce Ni maximum in presence of tetraethyl ammonium iodide. It is evident from the values, both in acid and neutral media the quinolones were active. Since the Ni maximum occur at —ve side of the ECM (—1.1V), we may expect in neutral medium the electron-rich quinolones not to suppress or eliminate the Ni maximum. But the results make one to understand that even —vely charged species attack —vely charged Hg drop. It has been reported[23] that a +vely charged colloid is attacked by +vely charged Hg drop. Comparison of both the results gives that the activity of a compound at the Hg snrface is not always governed by the charges alone. It is plausible that the charge attraction may help the adsorption process to a greater extent even though it is an aiding secondary process.

In acid medium almost all quinolones showed an immediate activity. This is understandable because the protonated species will be easily attracted by the —vely charged Hg drop. Hence along with physical adsorption, the coulombic type of adsorption also

TABLE—III **Current values in μA observed for Nickel Maximum**

Bulk Conc of Quinolone 10^{-3}M Ref. Table- I

SUPPORTING ELECTROLYTE								
	KCl				NH_4Cl			
Medium	N		A		N		A	
Vol. ml.	0	5	0	5	0	5	0	5
VQ	0.96	0	3.36	0	5.10	0	2.52	0
MVQ	1.14	0	3.0	0	5.58	0	2.64	0
MMVQ	1.02	0.6	2.88	0	5.88	0	2.88	0
MDVQ	0.84	0	3.06	0	7.20	0	2.94	0

aids the process. In NH_4Cl medium all the quinolones were active except that the current values were little bit higher than that of (KCl—neutral) medium. Changing the pH from neutral to acidic range the current values were found to be decreased.

From the foregone paragraph as well as keeping in view the work of Frumkin[25]. it is clear that adsorption takes place at the dropping Hg electrode and monolayers are formed. Mostly the nature of the layer immediately adjacent to the electrodeinterface is of prime significance in controlling the rate and the mechanism of electrode process[26].

Substances in general, which are adsorbed at the electrode solution-interface affect charge distribution at the boundary and can cause a reduction in the electrode area. It is evident that quinolones, like other surface active compounds get adsorbed at the electrode surface. The exact kinetics of these adsorption process is undertaken to understand more clearly the activities shown by these quinolones.

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