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Evaluation of Electrochemical Reduction of Chloroform by Drop Mercury Electrode

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In this work, the reduction wave of chloroform was studied by differential pulse polarography (DPP) and square wave voltammetry (SWV). The effects of supporting electrolyte and solvent were discussed. In DPP experiments, the reduction wave of chloroform was observable in aqueous solutions of tetramethylammonium bromide (TMABr) and tetraethylammonium bromide (TEABr) as the supporting electrolytes. Water, ethanol and dimethylsulfoxide (DMSO) were examined as solvents to find the most suitable solvent. Square wave voltammetry technique was chosen to study the quantitative parameters in different solvents. DMSO proved to be the best due to its sensitivity, reproducibility, limit of detection and strong interaction with chloroform. Cyclic voltammetry was employed in order to elucidate the electrode reaction mechanism. Bromoform was also studied and the differences between the electrode reaction mechanisms of chloroform and bromoform were distinguished.

Key Words: Chloroform, Differential pulse polarography, Square wave voltammetry, Cyclic voltammetry, Solvent.

INTRODUCTION

Chloroform is a toxic substance[1] which fluxes through environment mainly from chemical and pharmaceutical industries, water and wastewater treatment, seawater and soil processes and other natural processes[2].

Elucidation of the electroreduction mechanism of chloroform is a reaction of paramount importance both in synthesis and environmental treatment[3-6]. Furthermore, considering the advantages of electroanalytical techniques in organic analysis such as speed of analysis, cost, selectivity, sensitivity and ability in analysis of mixtures[7], sensitive polarographic techniques such as differential pulse and square wave could be considered for determination of chloroform in environmental samples instead of gas chromatography[8-11] and spectrophotometry[12-19] techniques which are commonly used in the quality control laboratories.

There have been a few reports on the electrochemical reduction of chloroform at the mercury drop electrode[20,21]. Fry *et al.*[20] investigated the behaviour of organic halides by differential pulse polarography to develop electrochemical determination and detection methods. This paper has considered a general mechanism for the reduction of organic halides, and related it basically to the type of solvent. Also, it has expressed only the theoretical aspects of the electrochemical determination of organic halides, but has not practically evaluated the method.

Recently, a broad research program was carried out on electroreduction of organic halides at the silver electrode surface by a research group[22-25] at the University of Milano, providing evidence of the extraordinary electrocatalytic properties of silver for organic halides. Considering the extraordinary affinity of silver for halide anions, they proposed different mechanisms for electroreduction of organic halides depending on the type of the halide group (*i.e.* Cl^-, Br^- or I^-). They suggested that the affinity of electrode for the halide group is a major determinant factor in the elucidation of the electroreduction mechanism. They compared the reduction mechanism on the silver (with high affinity for halides) with GC (with no affinity for halides) electrodes. However they did not consider the mechanism on the mercury drop electrode as an electrode substance with moderate affinity for halides[22-25].

On this basis, present research will concentrates on the study of the electrochemical reduction of chloroform at the mercury drop electrode. First, differential pulse polarography (DPP) is employed to find the suitable conditions. To discuss the possibility of determination of chloroform, due to its sensitivity, square wave voltammetry (SWV) is employed as the operating technique. Analytical parameters such as linear range, reproducibility and limit of detection are reported. SWV at a mercury drop is also evaluated as a reliable method for detection of chloroform instead of gas chromatography or spectrophotometry techniques.

Mechanistic investigations are performed using cyclic voltammetry. Also bromoform is studied to elucidate the effect of halide group on the mechanism of electroreduction of halomethanes at the mercury surface. The present results are in agreement with those obtained by Milano University Research Group[22-25].

EXPERIMENTAL

The solvents were dimethylsulfoxide with 99.9 % purity (Reidel), ethanol (Merck) and triple distilled water. Tetraethylammonium bromide (Kodak), tetramethylammonium bromide (Merck), potassium chloride, sodium acetate and sodium hydroxide (all from Riedel) were used as supporting electrolytes. Bromoform were purchased from Merck and chloroform from Riedel. All the acids were purchased from Merck Company. All the reagents were used as received, without further purification.

Stock chloroform solution was prepared daily by dissolving the proper amount of chloroform in 50:50 water-ethanol mixtures.

Polarographic investigations on the chloroform and bromoform were carried out by a polarograph instrument from EG&G Princeton Applied Research, model

384B electrochemistry system. Electrochemical cell consists of a Pyrex glass container with a working electrode, a Pt-wire counter electrode and a saturated Ag/AgCl reference electrode. The working electrode was the hanging mercury drop electrode (HMDE; model 303A, EG&G Princeton Applied Research). Polarograms were recorded by a DMP-40 HIPLOT recorder from Houston Instrument Company.

Procedure: The polarographic measurements were taken using the following procedure; 10 mL of supporting electrolyte solution (supporting electrolyte with known concentration in the desired solvent) was transferred to the polarographic cell and purged with helium gas (the purity was 99.99 %) for 800 s, then the proper amounts of chloroform were spiked using an eppendorf sampler and the polarograms were recorded by sweeping the electrode potential over a desired range with a suitable scan rate depending on the technique used. Further purging of the solution after spiking chloroform was avoided because chloroform is volatile and will escape during purging. Due to small volume of spiked chloroform, the oxygen present in the spiked solution did not perturb the polarographic analysis. During the analysis a blanket of helium gas was covering the solution to prevent oxygen introduction.

The values for instrumental parameters were as below: For DPP experiments; pulse height, 20 mV; drop time, 1 s; frequency, 100 Hz; scan rates were different in experiments and are mentioned for each special case in the article. For SWV experiments pulse height, 20 mV; equilibration time, 5 s and scan rate was 200 mV s^{-1}. For CV experiments scan rate was 33.33 mV s^{-1}. In all experiments the drop size was small.

RESULTS AND DISCUSSION

Effects of supporting electrolyte: A number of studies have demonstrated that the polarographic behaviour of alkyl halides is dependent upon the experimental conditions employed, and one of the significant variables is known to be the nature of the supporting electrolyte[20]. Thus in the first step five common supporting electrolytes were examined to find the most suitable one. The supporting electrolytes which were examined were potassium chloride, acetate buffer, sodium hydroxide, tetramethylammonium bromide (TMABr) and tetraethylammonium bromide (TEABr). The DP polarographic studies of the five samples showed no reduction wave for chloroform for three supporting electrolyte, namely, potassium chloride, acetate buffer and sodium hydroxide. This is due to the fact that they have a narrow potential window in the negative side. However, DPP experiments with TEABr and TMABr, proved them as suitable medium for study of chloroform. The present results for these supporting electrolytes show that their DP polarographic waves were broad and also the peak potential was not reproducible. This is an implication of characteristic irreversibility of DP polarographic wave of chloroform. In comparison, TMABr provides a more suitable electrolytic medium for study of chloroform in water (Fig. 1).

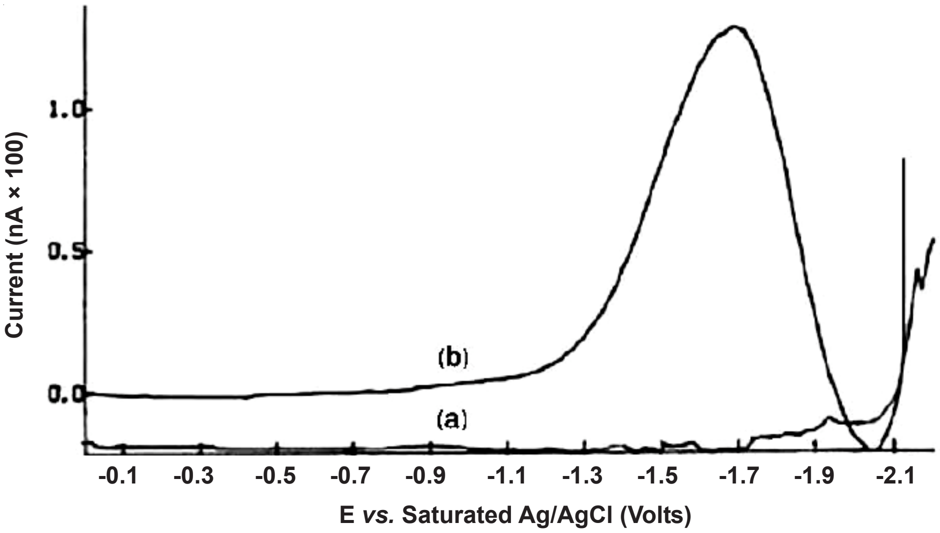

Fig. 1. DP Polarogram for (a) 10 mL supporting electrolyte (TMABr 0.025 M) and (b) 5 µL added chloroform in water. Pulse height was 20 mV and scan rate was 10 mV s^{-1}

It is a fact that the range of potential over which polarographic measurements can be made is limited by the decomposition potential (E_d) of the supporting electrolyte and this potential moves slowly toward more negative values as the size of the alkyl chain increases. Usually one expects supporting electrolytes of greater alkyl chain such as tetrabutylammonium bromide to be good candidates. However, further studies of the effect of supporting electrolytes with the alkyl chains greater than ethyl group were avoided due to the following reasons:

First, as the cation of supporting electrolyte increases in size, peak potential will undergoes a progressive displacement to more negative potentials. As a result, the wave of chloroform will become more drawn out of the accessible potential window and thus cannot be observed. Second, relative rate of electron transfer depends on the nature of the R group in the tetraalkylammonium ion, $R_4N^+X^-$, used as electrolyte: as R increased from methyl through heptyl, electron transfer becomes progressively slower. The electrolyte effect ought to be pronounced in the case of cathodic process in which electron transfer is very slow. And finally, the solubility of longer alkyl halide chain would be diminished in water.

The effect of supporting electrolyte concentration was also investigated. Experiments were carried out by using two different concentrations of supporting electrolyte: 0.025 M and 0.1 M. Using the higher concentration, DP polarographic peak potential shifts toward more positive values. Therefore higher concentration was preferred especially for quantitative analysis, because polarographic wave completely falls within the accessible range of potential window and the errors resulting from increasing background current at the limits of potential window would be eliminated.

Effects of solvent: The choice of solvent is often dictated by the solubility and reactivity of the material to be studied. As the main objective is the detection of chloroform in water, naturally water could be a choice. Although the solubility of chloroform in water is limited (0.8 g/100 mL), this limitation does not seem to be a serious one due to present interest in measuring the trace amounts of chloroform which is produced during disinfection process. On the other hand, this amount is considerably lower than detection limit of the method, so a preconcentration step is necessary prior to measurement by polarography. Common methods for pre-concentration of chloroform present in water involve extraction of chloroform to an organic solvent[26,27] or sorption of chloroform onto a solid sorbent (*e.g.* activated carbon[28,29] or polymeric resins such as Amberlite XAD-4[30]) and then elution by an organic solvent. Therefore measurement of chloroform by polarography should be performed in an organic or at least mixed organic/water media. In this regard, ethanol and dimethylsulfoxide (DMSO) were chosen as the organic solvents which are capable of eluting chloroform from the sorbent and the polarographic wave of chloroform was studied in these two solvents and the binary water-ethanol mixtures. Table-1 shows the data related to physical properties of the selected solvents and the characteristics of DP polarographic wave of chloroform in each solvent system. TEABr was chosen to study the effects of solvents because of the insufficient solubility of TMABr.

TABLE-1
DATA RELATED TO STUDY THE EFFECTS OF SOLVENT.
PHYSICAL PROPERTIES OF THE SOLVENT [Ref. 28] PEAK POTENTIALS
AND STATISTIC PARAMETERS AFFECTING QUANTITATIVE ANALYSIS

Solvent	Physical properties of solvent				Peak potential of chloroform	Linear regression equation
	Liquid range/oc	Vapour pressure†	Dielectric constant	Viscosity‡	E_p *vs.* Ag/AgCl (V)	
Water	0 to 100	3.2	78.4	0.89	-1.55	I (nA) = 451.88 C (μg mL^{-1})-218.81
Ethanol	-114 to 87	8.0	24.6	1.08	-1.76	I (nA) = 501.52 C (μg mL^{-1})+270.81
DMSO	19 to 189	0.0	64.4	2.50	-1.65	I (nA) = 2964.47 C (μg mL^{-1})+302.01

Solvent	Quantitative parameters							
	$S_{x,y}$	S_b	S_a	n	r	RSD (%)	LOD (μg mL^{-1})	Dynamic range (μg mL^{-1})
Water	168.18	10.66	142.14	7	0.9986	5	3.0	3.0-20.0
Ethanol	19.65	8.50	14.27	9	0.9990	12	0.3	0.3-3.0
DMSO	146.94	54.20	100.38	10	0.9987	2	0.3	0.3-2.7

†Vapour pressure in units of kPa; ‡Viscosity in units of 10^{-3} kg m^{-1} s^{-1}

Differences in peak potentials could be interpreted in two ways. First, the solubility of chloroform in water is lower than in dimethylsulfoxide and ethanol. This would be meaning that chloroform interactions are more with ethanol and DMSO. As the solubility of chloroform increases, the peak potential shifts towards more negative potential values. Second, negative shift may be due to differences in the dielectric constant. As the dielectric constant of solvent decreases, IR drop increases. As is evident in Table-1, order of decreasing dielectric constant is: water, DMSO and ethanol, which is consistent with the shift in the peak potential to more negative values.

Furthermore, important parameters relating to quantitative analysis in each solvent were studied. For quantitative analysis, parameters which are effective on sensitivity of measurements must be optimized. One of the main factors which has a significant influence is the drop size. In general, increasing the size of mercury drop will improve the sensitivity. Higher currents were observed as the size of drop increased, but on the other hand, the width of the wave increased and as a result a part of polarographic wave fell out of the accessible potential window, and some errors occured in quantitative analysis, therefore a small drop was preferred.

Because of the higher sensitivity of the square wave technique in comparison with the differential pulse technique, it is preferred to perform quantitative analysis by this method.

For comparison we studied calibration curves in different solvents using TEABr as the supporting electrolyte. Line regression equation, standard error ($S_{x,y}$), standard deviations of the slope (S_b), intercept (S_a) and the number of data points (n) are listed in Table-1.

In water with 800 s of purging the solution, the chloroform wave disappears. This means that purging will decrease the chloroform concentration in the solution to below the detection limit of the method. Purging for shorter durations will decrease the peak current gradually.

In ethanol, it was observed that during the purge time, solvent volume gradually reduced which is due to high vapour pressure of ethanol. The purge gas may be presaturated with solvent, but when the vapour pressure is high; it is often difficult to maintain constant composition and temperature because of solvent evaporation[31], and this will cause serious errors in quantitative analysis which decreases the accuracy and reproducibility of the results. Thus, when working with ethanol it is preferred to reduce purge time to 240 s to avoid considerable solvent loss.

In DMSO, purging even for as long as 800s did not affect the peak current (and thus the chloroform's concentration). This phenomenon is related to the strong interactions between chloroform and DMSO, which retains the chloroform in solution. As is evident in Table-1, this great advantage along with higher sensitivity, lower detection limit, better reproducibility and the ability to elute chloroform from sorbents, makes the dimethylsulfoxide an ideal solvent for a real sample analysis.

In order to study the effects of the composition of ethanol-water binary mixtures, experiments were carried out using TMABr as the supporting electrolyte in these binary solutions with different compositions. It was impossible to perform experiments in pure ethanol, because of insufficient solubility of TMABr in ethanol. Table-2 shows the values of peak potentials for chloroform in different compositions of ethanol-water mixtures. The results showed that the potential window will decrease as the ethanol/water ratio in solvent mixture increases. The peak potential (E_p) however, shifts to more negative values as the ethanol/water ratio increases in EtOH-H_2O binary solutions, except for pure water in which E_p is more negative than 20:80 ethanol/water binary solutions. This could be related to strong interactions between ethanol and water.

TABLE-2
PEAK POTENTIALS IN DIFFERENT COMPOSITION OF MIXED ETHANOL-WATER SOLVENTS *vs.* SATURATED Ag/AgCl

Ethanol:water (% v/v)	Concentration (μg mL^{-1})				
	20	40	60	80	100
	Peak potential *vs.* Ag/AgCl (V)				
0:100	-1.64	-1.67	-1.68	-1.68	-1.66
20:80	-1.58	-1.61	-1.61	-1.63	-1.64
40:60	-1.61	-1.64	-1.64	-1.65	-1.67
60:40	-1.67	-1.67	-1.68	-1.69	-1.69
80:20	-1.80	-1.85	-1.87	-1.87	-1.89

In binary mixtures of ethanol-water, the loss of solvent during purging time was considerably lower compared to pure ethanol and thus reproducibility is improved.

Mechanistic investigations: The cyclic voltammograms obtained in this experiment reveal irreversible polarographic waves for chloroform in water (Fig. 2). In order to show the reaction mechanism more clearly, a screening analysis of the shift of current and peak potential values with varying scanning rate was performed. The results showed that I_p *vs.* $\nu^{1/2}$ is linear (Fig. 3), while E_p progressively increases with ν, which is the characteristic of a totally irreversible process.

The mechanism of the reduction of alkyl halides may differ upon electrode material, solvent and somewhat electrolyte type. The reduction of halogenated organic compounds involves the cleavage of carbon-halogen bonds.

In the case of chloroform in aqueous medium the mechanism of reduction consists of a two electronic reduction step for chloroform:

$$\mathrm{CHX_3 + e^- \rightarrow [CHX_3^{\bullet -}] \rightarrow [CHX_2^{\bullet}] + X^-}$$

$$\mathrm{[CHX_2^{\bullet}] + e^- \rightarrow [CHX_2^-]}$$

$$\mathrm{[CHX_2^-] + H_2O \rightarrow CH_2X_2 + OH^-}$$

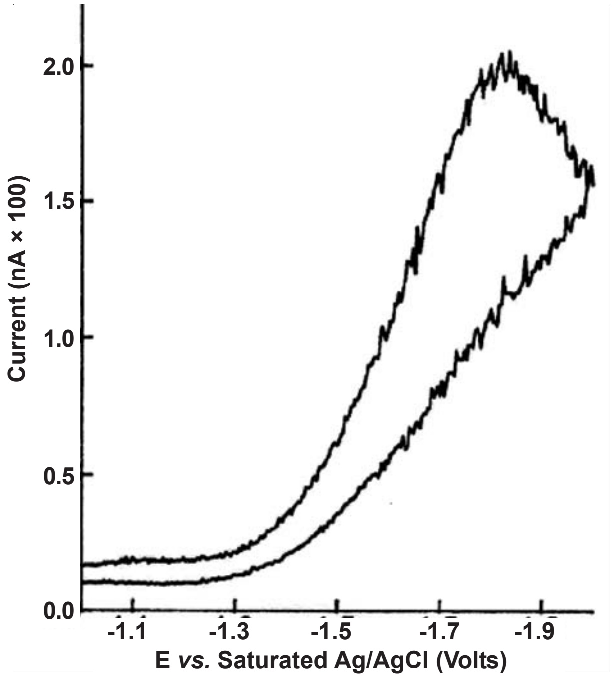

Fig. 2. Cyclic voltammogram for 5 µL added chloroform in 0.1 M TMABr as supporting electrolyte in water. Scan rate was 33.33 mV/S

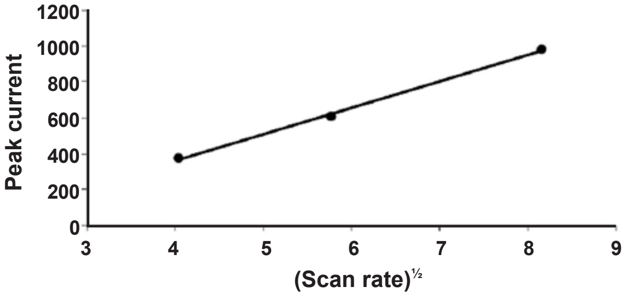

Fig. 3. Plot of peak current (mA) *vs.* (scan rate, mV s^{-1})$^{1/2}$

The reduction process can be continued until methane molecules have been formed[21].

$$CHX_3 \rightarrow CH_2X_2 \rightarrow CH_3X \rightarrow CH_4$$

Each step involves a two electronic reduction which is totally irreversible. Therefore, it is expected to observe three polarographic waves for chloroform. Indeed in the case of chloroform the next steps fall beyond the negative limit of the potential window and thus could not be observed. For electrodes with highly electrocatalytic properties such as silver, which has peculiar affinity for halogens, the mechanism would be diverted to a mono electronic reduction process.

In order to elucidate reaction mechanism, investigations on bromoform reduction were performed in aqueous medium using 0.1 M TMABr as supporting electrolyte. The results of DPP experiments show that bromoform is reduced on mercury drop electrode giving three irreversible polarographic waves at potentials: -0.38, -1.44 and -1.76 V. As cited earlier, the results are as expected. Bromoform could be reduced electrochemically to methane and bromide ion.

The expected mechanism predicts three steps:

$$CHBr_3 \rightarrow CH_2Br_2 \rightarrow CH_3Br \rightarrow CH_4$$

Studies also carried out in ethanol solution using 0.1 M TEABr. A negative shift in reduction potential is expected and observed as cited earlier. Here only two waves are observed and the third peak falls beyond the accessible range of the potential window, which is due to negative shift of the waves in ethanol and therefore could not be seen. The remarkable shift in peak potential for the first polarographic wave of bromoform with respect to chloroform could not only be related to difference in activity of C-X bond, and must be related to other reasons.

We correlate this phenomenon to difference in mechanisms. In fact, halide sorption[22-25] on mercury surface takes place at negative potentials. This phenomenon will result in: (1) A remarkable shift (ranged from 0.4 to 1.2 V) in the positive direction of the reduction potentials. (2) A cage effect, resulting in the promotion of intermolecular *versus* intramolecular reactions, which strongly depends on the state of the surface.

Both the above-mentioned effects were explained on the basis of an ‘attenuated radical intermediate’ R···X···Hg, whose reactivity was found to be modulated by the active surface and by the supporting electrolyte[23].

The affinity of mercury for halides is: I > Br > Cl. The first reduction peak for chloroform occurs in about -1.6 V, while for bromoform the first peak was observed in about -0.3 V. Such a great difference in reduction activity could not only be related to activity of C-X bond. As expected, the general order of reactivity for leaving halide group (I > Br > Cl) is also retained in mercury, but the reactivity of C-Br is so enhanced in comparison with C-Cl bond, that it seems some additional factor must have interfered. Presence of auxiliary groups in the substrate structure will improve the adsorption effects and shift the reduction potential to more positive values[23,24]. Here, the larger affinity of mercury for bromine and the presence of three bromide group will considerably improve the adsorption of bromoform on mercury. Thus the mechanism changes somewhat in respect to chloroform and the ‘attenuated radical intermediate’ will prevail the previous mechanism mentioned for chloroform.

With the proposed mechanism, presence of halide group in the media (in supporting electrolyte or as added halide) will causes the peak potential to shift towards more negative values. This could be explained (a) in terms of reversed IHP charge, which heavily affects the activation energy profile at the electrode/solution interface, (b) and/or in terms of specific adsorption competition between the bromide substrate to be reduced and the supporting electrolyte ions present on the IHP: it is reasonable that C-X reaches the electrode surface more easily when an adsorbed alkylammonium cation must be displaced (*i.e.* when working with tetrafluoroborate or perchlorate salts) than when a more strongly specifically adsorbed halide (I > Br > Cl) must be displaced.

Cyclic voltammograms (Fig. 4) confirm the results of differential pulse polarography studies. The cyclic voltammograms are evident for electrocatalytic activity of mercury, which is the result of specific adsorption on mercury and reveals more aspects of the differences in the reduction mechanism of chloroform and bromoform. Table-3 indicates the characteristics of each polarographic wave related to progressive number of cycles in aqueous media and in the presence of TMABr as supporting electrolyte. Only information of the last cycle is recorded. As is evident in Table-3, three polarographic waves are observed in the first cycle but in the second to fifth cycles the first wave is less pronounced and the E_p shifts toward more negative potentials by the increase in the number of the cycles. This situation is quite different for chloroform in many aspects. For chloroform, progressive cycles did not differ considerably in E_p or I_p, while here the first wave attenuates considerably and the second wave shifts toward more negative potentials as the number of cycles would increase.

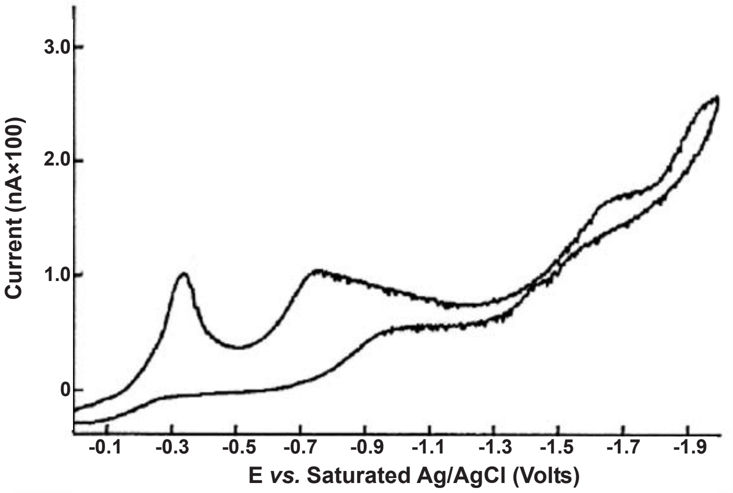

Fig. 4. Cyclic voltammogram for bromoform in 0.1 M TMABr as supporting electrolyte in water. Scan rate was 33.33 mV s^{-1}

By proposed mechanism, cyclic voltammograms could be interpreted. In the first cycle which mercury is formed freshly, there are lots of active sites in mercury and bromoform reaches the surface easily, thus three peaks are observable for bromoform as DPP experiments showed. As the time elapsed, the bromide present in supporting electrolyte poisons the surface of the mercury and so it will be hard for

TABLE-3
EFFECT OF PROGRESSIVE CYCLES ON PEAK POTENTIALS AND PEAK CURRENTS

		Cycle number				
		Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
Peak 1	I_{p1} (nA)	80	16	16	16	16
	E_{p1} (V)	-0.34	-0.30	-0.30	-0.30	-0.30
Peak 2	I_{p2} (nA)	56	84	111	185	195
	E_{p2} (V)	-0.74	-1.2	-1.30	-1.45	-1.60
Peak 3	I_{p3} (nA)	22	–	–	–	–
	E_{p3} (V)	-1.65	–	–	–	–

– Out of accessible range of potential window.

bromoform to reach the surface. Considerable reduction in I_{p1} and considerable shift in negative direction for E_{p2} strongly support this hypothesis. Such differences in progressive cycles could not be observed for chloroform which does not obey such mechanism.

Conclusion

Polarography is applicable as a reliable, rapid and simple method for detection of chloroform. The results showed that dimethylsulfoxide is an ideal solvent for determination of chloroform. The main advantages of this method compared to the other methods such as gas chromatography or spectrophotometry are simplicity, speed, low risk and low cost.

Investigations on the mechanism of the electrode reaction showed some differences between the electrode process for chloroform and bromoform arising from the improved affinity of mercury for bromine compared to chloroform and the presence of two auxiliary bromine atoms in the bromoform structure, which intensifies the effect and somewhat alters the mechanism of reduction from a two electronic process to a monoelectronic process. More investigations are needed to prove these hypotheses which are left for future studies.

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