SQUARE-WAVE VOLTAMMETRIC DETERMINATION OF SALOPHEN

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Abstract

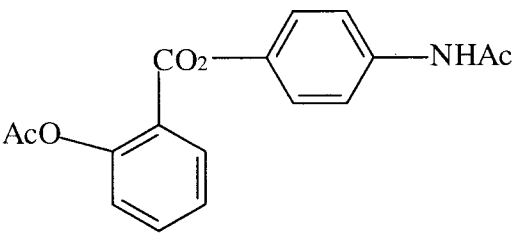
A square-wave voltammetric method for quantitative determination of salophen at a stationary mercury drop electrode is developed. Salophen (4-acetylamid) phenyl ester) is a compound which creates a large number of complexes with heavy metals. These complexes are widely used in the chemistry as well as in medicine. Salophen is a surface active compound. It undergoes quasireverzible reduction on the HMD electrode within the potential range from –1.20 to –1.55 V vs Ag/AgCl (saturated KCl). The optimization of the experimental parameters was achieved. The optimal conditions for quantitative determination of salophen are: 0,1 mol/L ammonia buffer with pH = 9.15 as a supporting electrolyte, frequency of 120 Hz, amplitude of 20 mV, scan increment of 4 mV and accumulation potential of –1.00 V. The detection limit of salophen was 5.13×10^{-7} mol/L. The reproducibility of the method expressed in the therm of the relative standard deviation varied from 0.4 to 3.5 %.

Key words: Square-wave voltammetry, salophen.

1. Introduction

The demand for the detection of trace levels of substances of environmental, clinical and forensic significance is growing tremendously. Electroanalytical techniques such as square-wave voltammetry (SWV) and cyclic voltammetry have become indispensable tools in modern analytical chemistry. These techniques are widely used for the study of electrochemical behaviour as well as for quantitative determination of various substances [1-3]. In this paper square-wave voltammetry is used for quantitative determination of salophen. Salophen (4-acetylamino) phenyl ester (figure 1) is a pharmacologically active compound.

Figure 1. Molecular structure of salophen



This substance is a constitutional part of the drugs which are based on salycilates [4]. Its chemical structure contributes to building a large number of complexes with metals such as cobalt, manganese, uranium, etc. These complexes are widely employed in different fields. So, the complex of salophen with uranium named uranyl salophen is used as a building material of some anion selective membranes [5], while the complex of salophen with

manganese (III) is used as a therapeutic agent in the selenite cataract model [6]. The electrochemical properties of salophen are not investigated so far.

2. Experimental

All chemicals were of analytical grade. The stock solution of salophen was prepared by dissolving an appropriate amount of salophen in glacial acetic acid. All experiments were performed at Polarographic Analyzer Princeton Applied Research Model 384 B. The working electrode was a hanging mercury drop (HMDE), Ag/AgCl (saturated KCl) was a reference while Pt wire was a counter electrode. All experiments were achieved at room temperature.

3. Result and discussion

In order to reach the best sensitivity and peak definition, firstly a preliminary study about the electrochemical behaviour of salophen in ammonia buffers with different pH as well as in 1mol/L KOH was completed. The results for the peak current i_p, peak potential $E_p$as well as for the half-peak width $\Delta E_{p/2}$ are listed in the Table I.

Table I. Dependence of the peak potential, peak current and half-peak width on the pH of supporting electrolyte. c (salophen) = 5×10^{-5} mol/L, frequency f = 120 Hz, amplitude E_{sw} = 20 mV, scan increment dE = 4 mV.

Supporting electrolyte				
0.1 mol/L ammonia buffer				
pH	i_p/μA	E_p/V	$\Delta E_{p/2}$/mV	$i_p \times 10^3 / \Delta E_{p/2}$ /μA mV^{-1}
8.9	1.086	-1.492	110	9.87
9.15	1.289	-1.436	100	12.89
9.9	0.932	-1.364	115	8.1
10.35	1.05	-1.36	120	8.75
10.55	0.86	-1.356	140	6.14
11.1	0.692	-1.324	170	4.07
1mol/L KOH	1.078	-1.192	140	7.7

It can be seen that with an increase of pH, the peak potential E_p shifted towards more positive values which implicates that the H_3O^+ ions are involved in the electrochemical process. The ammonia buffer with pH of 9.15 was selected as most suitable because the reduction peak obtained showed the highest sensitivity and the best definition. The SWV response of salophen recorded in 0.1 mol/L ammonia buffer is a single peak, well defined with a half-peak width $\Delta E_{p/2}$ of 100 mV.

The molecules of salophen has shown adsorption properties on the surface area of the working electrode. The adsorption isotherm of salophen is presented in figure 2. It can be seen that the saturation of the electrode area with molecules of salophen was reached at the accumulation times grater than 45 s. These properties of salophen molecules can be employed for its quantitative determination at a trace level after the preconcentration step.

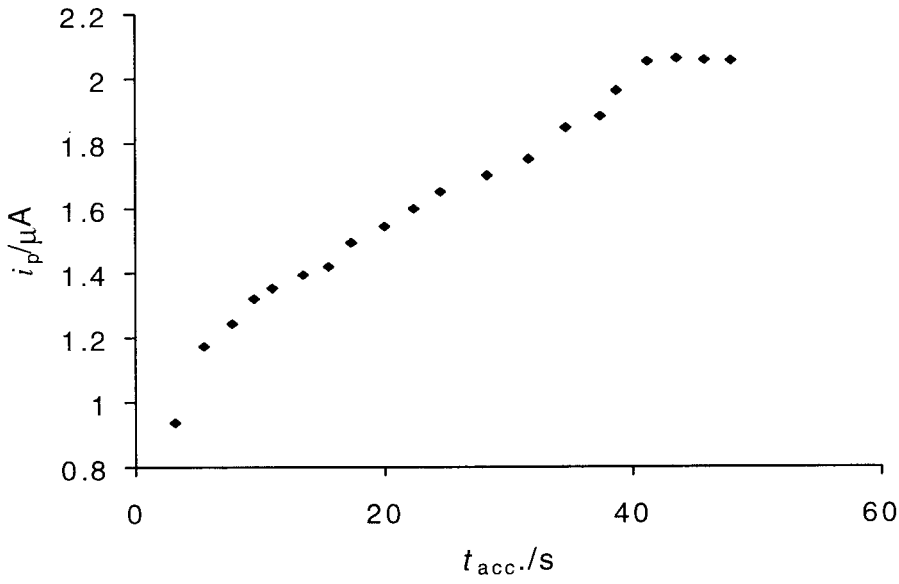


Figure 2. Dependence of the peak current on the accumulation time. c(salophen) = 5×10^{-5} mol/L, frequency f = 120 Hz, scan increment dE = 4 mV and amplitude E_{sw} = 20 mV. Supporting electrolyte was 0.1 mol/L ammonia buffer with pH = 9.15.

In order to investigate the influence of the adsorption strength of salophen molecules to its voltammetric response, a certain amount of methanol was added to the supporting electrolyte. It is well known that methanol molecules adsorbs itself on the electrode surface, competing with the adsorption of salophen molecules, and thus changes the adsorption constant of salophen. The effect of methanol on the peak current of SW peak of salophen is presented in the Figure 3. Part of the curve in Figure 3 is parabolically shaped with maximum located at 8 % (v/v) methanol. So, the addition of 0.8 mL methanol in a supporting electrolyte of polarographic cell significantly enhances the sensitivity of the method. In the same time, an increase the amount of methanol shifts the peak potential toward more negative values.

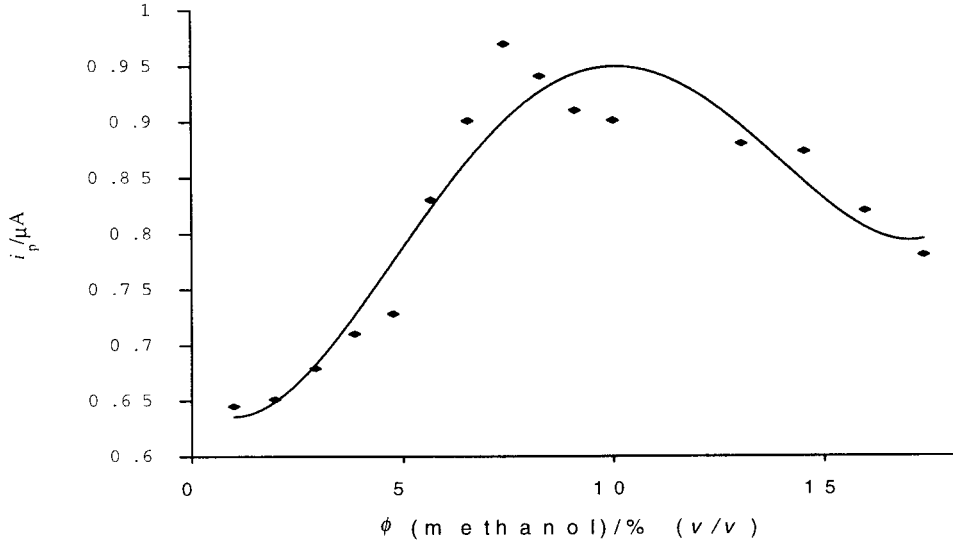


Figure 3. The influence of methanol on the SW peak current. Accumulation time $t_{acc.}$ = 15 s. All other conditions as in Figure 2

The influence of the SW frequency f on the peak current was studied between 10 and 120 Hz. A value of 120 Hz was chosen as suitable because it provided the highest peak current. The peak potential showed light shifts to negative values when the frequency was increased.

The influence of the SW amplitude E_{sw} on the peak current was studied between 10 and 100 mV and a non-linear relationship was observed in this range. The value of 30 mV was selected as optimum because it gave the largest ratio between peak current and half-peak width. An increase of E_{sw} more than 60 mV produced distortion in the voltammetric response and shifts in E_p towards positive potentials.

From an analytical point of view, the SWV is a powerful technique enabling determination of salophen at trace level. A linear calibration plot was constructed at a concentration level of 10^{-6} mol/L with a correlation coefficient of $R^2 = 0.992$ (figure 4). The detection limit is about 5×10^{-7} mol/L. The reproducibility of the results in the term of relative standard deviation range from 0.4 to 3.5 %.

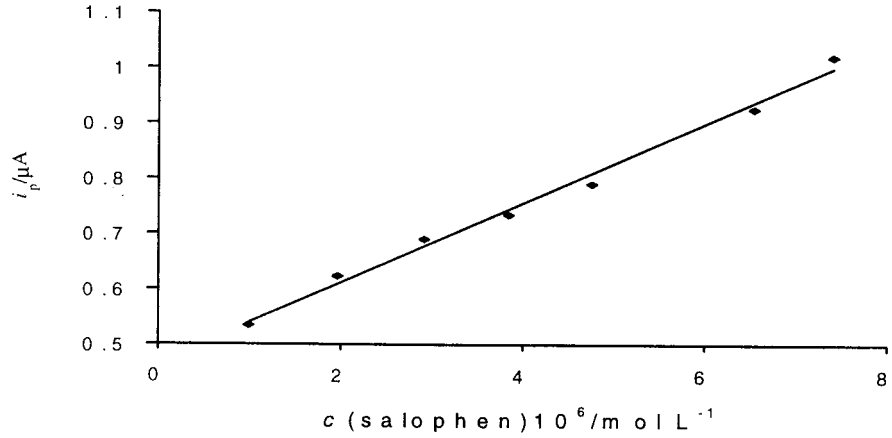


Figure 4. Calibration curve for salophen. Supporting electrolyte was composed by 9.2 mL 0.1 mol/L ammonia buffer with pH = 9.15 and 0.8 mL methanol. Accumulation time was 30 s. All other conditions as in Fig. 2.

4. References

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