

## SHORT COMMUNICATIONS

### PHASE SELECTIVE ALTERNATING CURRENT POLAROGRAPHY OF GOSSYPOL IN METHANOL

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**ABSTRACT.** Phase selective alternating current polarography of gossypol in buffered methanol solutions has revealed a hitherto unreported wave at  $-0.303$  V vs. Ag/AgCl/KCl (Sat'd in methanol). Some characteristics of this new wave are presented.

#### INTRODUCTION

Gossypol (Fig. 1) is a hexahydroxy-substituted binaphthaldehyde compound found in cottonseed. It has been demonstrated to have an antifertility action in males (1) and may be analytically determined spectrophotometrically (2), or using HPLC (1,3), as well as by other methods. Recently (4), an electrochemical study of gossypol in methanol was reported, in which earlier references about various chemical studies on it are mentioned. The electrochemical investigations referred to above (4) are mainly concerned with dc polarography, triangular wave voltammetry, controlled potential coulometry, and uv-visible spectrophotometry. It was found that the two aldehydic functional groups on gossypol are electrochemically reduced irreversibly to the alcohols; a mechanism was also proposed for the reduction.

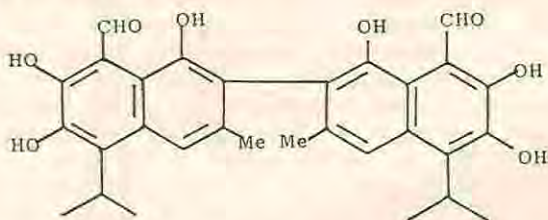


Fig. 1 Chemical structure of gossypol.

In the course of our study on the determination of gossypol in cottonseed oil, we applied the techniques of normal and differential pulse (dp) polarography as well as phase selective ac polarography, and we report in this paper the results found using the latter technique. Although both ac and dp polarography were found useful for the analysis of gossypol, this aspect of the work is not discussed here; rather, the hitherto unreported tensammetric behaviour of the compound will be presented.

#### EXPERIMENTAL

Polarographic studies were made using the Metrohm E505/506 Polarecord.

Phase selective ac polarograms were recorded on a dropping mercury electrode at phase angles of both  $\phi = 0^\circ$  and  $\phi = 90^\circ$ , and a frequency of 75 Hz. All potentials are reported relative to the silver/silver chloride/ saturated KCl in methanol reference electrode. The gossypol-acetic acid complex (Sigma chemical Co.) was used as such without further purification. Buffered methanolic solutions of pH = 9, using succinic acid (BDH), sodium methoxide and tetrabutylammonium perchlorate (Alfa Chemicals), were prepared as described in (4). All studies are reported at the single pH of 9.0 and at an ambient temperature of 20°C. The polarographic cell was deaerated with helium gas saturated with methanol prior to recording polarograms, and was also blanketed with a stream of this gas during measurements.

## RESULTS AND DISCUSSIONS

The fundamental harmonic ac polarogram ( $\phi = 0^\circ$ ) of gossypol in buffered methanol is shown in Fig. 2. As it can be seen, other than the reduction wave at  $E = -1.403$  V, there appears another wave at a potential  $E = -0.303$  V. This latter wave was believed to be an adsorption wave, and hence ac polarograms at  $\phi = 90^\circ$  were recorded. Under such conditions, the current is proportional to the electrical double layer capacitance. These polarograms (or tensammetric curves) are shown in Fig. 3 for different concentrations of gossypol. The peak currents were dependent on concentration, and, as expected (5), the dependence was not totally linear over the entire concentration range, see Fig. 4, but rather tended towards a plateau at higher concentrations. An analytical use of the adsorption wave at low concentrations is thus hinted. This may prove useful in studies at lower pH's when the reduction wave appears fairly close to the wave due to the supporting electrolyte.

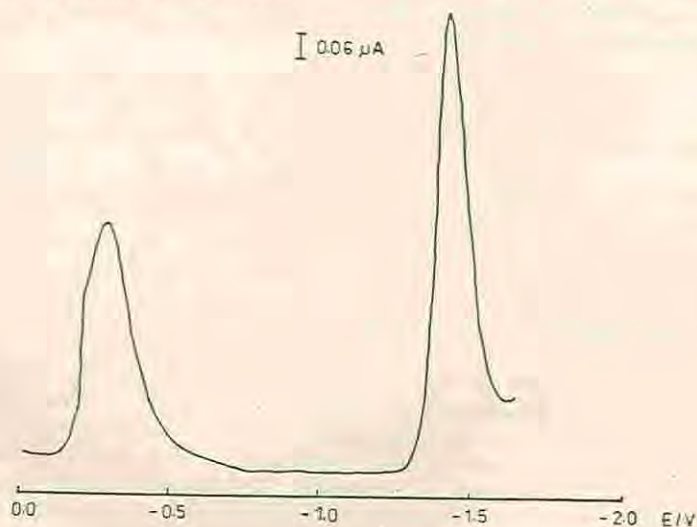


Fig. 2. Ac polarogram ( $\phi = 0^\circ$ ) for 1.0 mM gossypol in buffered methanol (pH 9.0).

No significant wave was observed under normal dc polarographic conditions thereby excluding the possibility that this new wave may have been due to a

faradaic reaction. A faradaic reaction causing the appearance of the peak at  $-0.303$  V is also excluded by the ac polarogram at  $\phi = 90^\circ$  since the reduction wave at  $-1.404$  V under such conditions is completely different in both magnitude and shape from that at  $-0.303$  V.

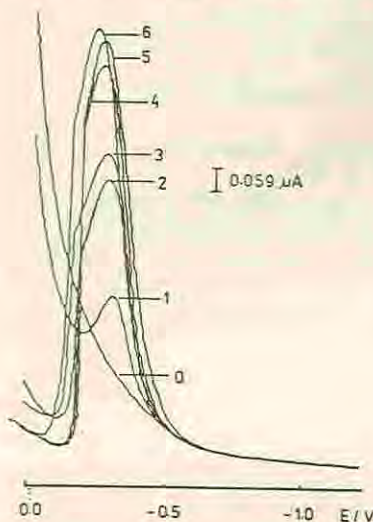


Fig. 3. Ac polarogram ( $\phi = 90^\circ$ ) for different concentrations of gossypol in buffered methanol (pH 9.0). 0) supporting electrolyte only, 1) 0.01 mM gossypol, 2) 0.05 mM, 3) 0.07 mM, 4) 0.1 mM, 5) 0.3 mM, 6) 0.5 mM.

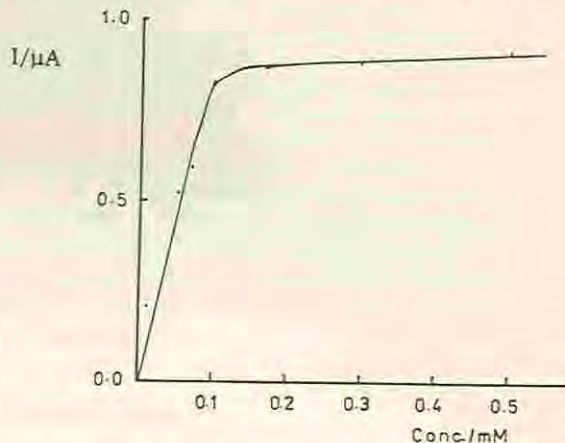


Fig. 4. Peak current (from ac polarogram at  $\phi = 90^\circ$ ) as a function of concentration of gossypol.

Attention may be drawn to the non-symmetrical shape of the adsorption wave. Repeated recordings with fresh solutions still revealed the sharp discontinuity or shoulder at high concentrations of gossypol. Examination of the potential region under differential pulse polarographic conditions also showed a very sharp peak at the region of discontinuity. According to Damaskin et al. (6), the shape of an adsorption wave, as reflected in capacitance-potential plots, is dependent on the magnitude of the particle-particle interaction parameter and discontinuities may appear for certain values of the parameter. These discontinuities have been associated with co-adsorption, interfacial condensation, or phase transitions (7,8). However, in order to examine any possible relation between the peculiar shape of the wave observed here and interfacial condensation or otherwise, it is believed that further experimental work on a hanging mercury drop may shed some light since, unless sufficiently long times are used, studies on the DME may prove difficult in order to gain insight on the equilibrium double layer properties from capacitance measurements (7). Also, studies with different supporting electrolytes and at different temperatures may prove enlightening. Work is in progress to unravel this issue.

#### ACKNOWLEDGMENTS

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## REFERENCES

1. M. -Z. Wang, *J. Ethnopharmacology*, **20**, 1 (1987).
2. A. Admassu and B.S. Chandravanshi, *Anal. Chem.*, **56**, 30 (1984).
3. S. Asmelash and E. Dagne, Abstracts of the Fifth Annual Congress of the Chemical Society of Ethiopia, 12-13 August, 1988, p. 20.
4. R.D. Braun, *Electrochim. Acta*, **32**, 459 (1987).
5. A.M. Bond, *Modern Polarographic Methods in Analytical Chemistry*, M. Dekker, N.Y., 1980, p. 367.
6. B.B. Damaskin, O.A. Petrii and V.V. Batrakov, *Adsorption of Organic Compounds on Electrodes*, Plenum, N.Y., 1971, p. 109.
7. R. Srinivasan and R. de Levie, *J. Electroanal. Chem.*, **206**, 307 (1986).
8. C. Buess-Herman, L. Gierst, M. Gonze, and F. Silva, *J. Electroanal. Chem.*, **226**, 267 (1987).