

Electroactive Monolayers of an Amphiphilic Quinone on Glassy Carbon Surfaces

Min D. Liu and Charles R. Leidner*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47906 U.S.A.

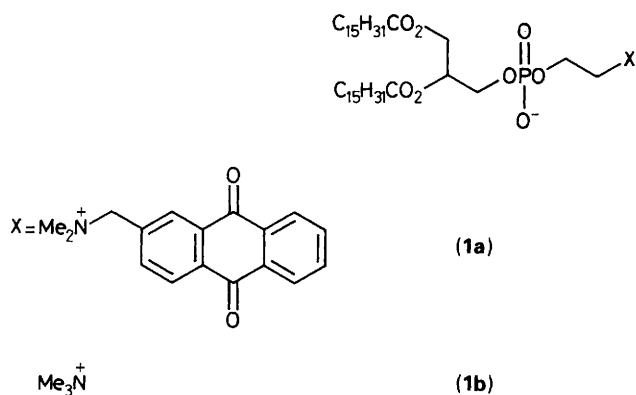
Amphiphiles from quinone-functionalized liposome solutions spontaneously adsorb onto glassy carbon electrodes to form electroactive, monolayer deposits.

The pursuit of organized molecular assemblies with controllable physical and chemical properties has entailed the preparation and characterization of liquid crystals, amphiphilic monolayers, vesicles (liposomes), and micelles.¹ Recent developments in this field have included the preparation and characterization of electroactive assemblies,²⁻⁵ particularly those immobilized on electrode surfaces.³ Herein, we report that amphiphiles (**1**) from quinone-functionalized liposomes⁴ spontaneously adsorb onto glassy carbon electrodes to form electroactive, monolayer deposits. Our primary interest in amphiphilic quinone assemblies is in the utility of quinone-functionalized liposomes as models of mitochondrial and thylakoid membranes,⁶ however the present assemblies are part of our continuing study⁷ of quinone films on electrode surfaces.

Quinone-functionalized liposomes can be prepared⁴ by sonication of the phospholipid quinone (**1a**) with the simple phospholipid (**1b**). The quinones within these liposomes can be reduced⁴ readily by external $S_2O_4^{2-}$ and reoxidized^{4b} by external $Fe(CN)_6^{3-}$. Considering this facile redox chemistry in the light of the report² of direct electrochemistry of heptylvio-

ogen within phosphatidylcholine liposomes, we reasoned that our quinone-functionalized liposomes would be interesting systems for electrochemistry. The cyclic voltammetric response of a 10 mmol (**1a**)/(**1b**) [6.0 mol% (**1a**)] liposome solution at a glassy carbon electrode is illustrated in Figure 1(A). The quinone/hydroquinone couple at *ca.* -0.6 V vs. standard calomel electrode (S.C.E.) is evident in this voltammogram. The shapes of the voltammetric waves and their dependence on scan rate suggest an electrocatalytic (or mediation) step. Voltammetric waves (-0.54 and -0.63 V) persist even after the electrode is rinsed and placed in a solution without liposomes [Figure 1(B)]. Clearly, adsorption plays a role in the voltammetry of the quinone-functionalized liposome solutions. An adsorbed, electroactive quinone deposit mediating the reduction of liposome-bound quinones would yield a pronounced increase in the cathodic peak current over the anodic peak current at slow scan rates, as observed in Figure 1(A).

The phospholipid amphiphiles spontaneously adsorb onto the glassy carbon electrode to form electroactive deposits even in the absence of the repetitive scanning used in Figure 1(A).



Dipping a glassy carbon electrode into an 8.8 mol% **(1a)**/**(1b)** liposome solution at open circuit for 10.5 min, rinsing, and placing it into a solution without liposomes results in the voltammetric response shown in Figure 1(C). The wave at -0.54 V decreases with successive scans, so that after 15 scans [--- in Figure 1(C)] a double-peaked voltammogram, identical to that obtained from successive scanning in the liposomes solution [Figure 1(B)], remains. The evolution of the voltammogram shown in Figure 1(C) is linked to the reduced form of the film, since holding the potential of a freshly-prepared film at -1.0 V for 1 min results in the same double-peaked voltammogram.

The voltammetric waves of a freshly-prepared film [*e.g.*, — in Figure 1(C)] possess equal anodic and cathodic peak currents, equal anodic and cathodic coverages (area under curves), and minimal peak splitting (*ca.* 20 mV), as expected for a surface-immobilized redox couple.⁸ The surface coverage of the electroactive quinones on the electrode in Figure 1(C) is 1.1×10^{-10} mol cm⁻² based on a two e⁻ couple. The measured coverage depends on length of dip-coating time and on mol% **(1a)** in the liposome solution. During our limited, initial studies we have observed coverages ranging from 0.25 to 1.9×10^{-10} mol cm⁻². Conversion of these coverage values to corresponding numbers of monolayers of amphiphiles is complicated by two factors. First, since the adsorption isotherms may be different for **(1a)** and **(1b)**, the mol% **(1a)** on the electrode may differ from that in the liposome solution. Second, the equivalent area of an amphiphile on the electrode is unknown, since the orientation of the amphiphiles (conceivably ranging from randomly dispersed on the surface to oriented perpendicular to the electrode surface as with organized monolayers³⁸) is unknown. Using CPK (Corey-Pauling-Koultou) models with known phospholipid dimensions⁹ as calibration, we estimate that a **(1a)** amphiphile adsorbed in a 'head-down' fashion occupies *ca.* 90 Å². A densely-packed monolayer of **(1a)** would thus correspond to a coverage of *ca.* 1.8×10^{-10} mol cm⁻². Incomplete adsorption of **(1a)** or concomitant adsorption of **(1b)** would lead to lower measured coverages, as observed with our system. Dipping a carbon electrode first into a **(1b)** liposome solution before dipping into a **(1a)**/**(1b)** liposome solution results in *ca.* 50% of the anticipated coverage of quinone, indicating that **(1b)** amphiphiles also adsorb onto the electrode. Prolonged immersion in a 15.8 mol% **(1a)**/**(1b)** liposome solution leads to a maximum coverage of quinone of 1.9×10^{-10} mol cm⁻²; this value is consistent with a 100 mol% **(1a)** monolayer coating. This result and that obtained from first dipping in a **(1b)** liposome solution suggest that **(1a)** adsorbs preferentially over **(1b)**. Our systems seem best described as monolayer films of **(1a)** and **(1b)**, whose coverage and/or mol% of **(1a)** can be manipulated by coating time and liposome composition.

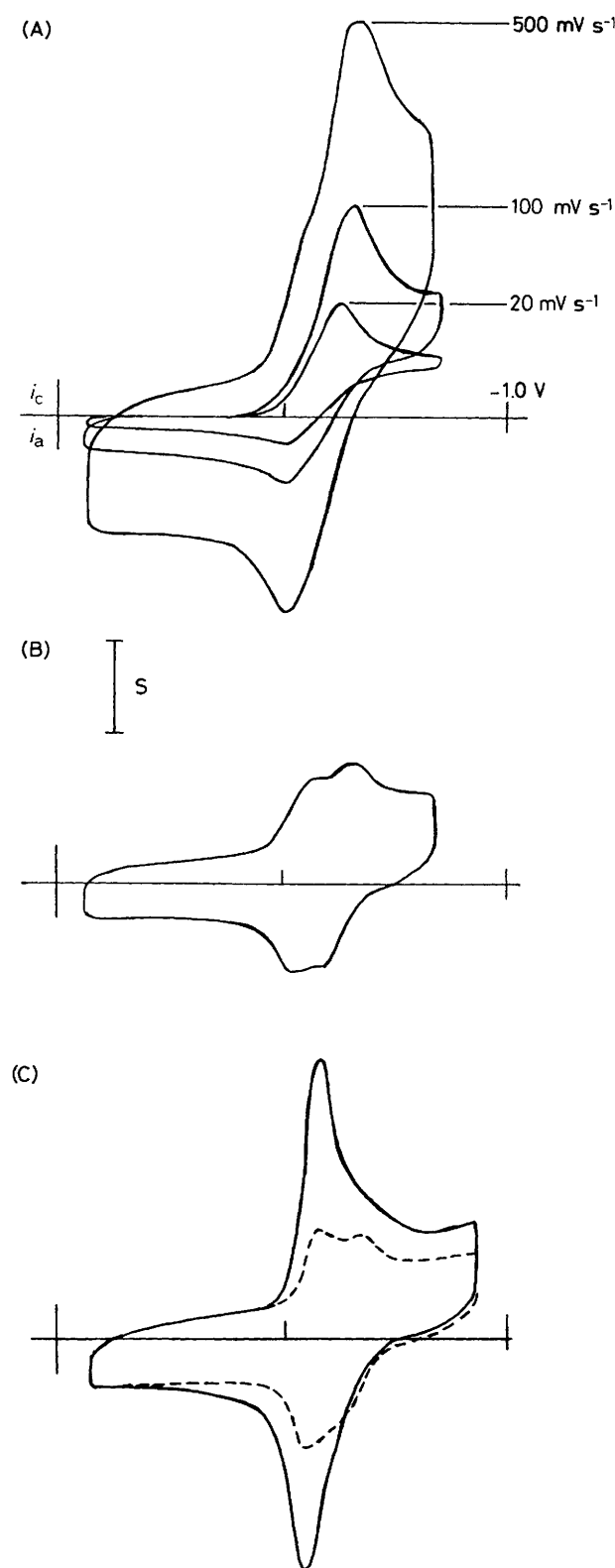


Figure 1. Cyclic voltammetric response of a glassy carbon electrode at 52 °C in a 0.2 M KCl solution with 0.05 M phosphate buffer (pH = 8); $S = 28.3 \mu\text{A cm}^{-2}$. (A) 10 mm **(1a)**/**(1b)** [6.0 mol% **(1a)**] liposome solution; scan rates = 500, 100, and 20 mV s⁻¹. (B) Electrode from (A) in a solution without liposomes; 200 mV s⁻¹. (C) Electrode, dip-coated in a 10 mm 8.8 mol% **(1a)**/**(1b)** liposome solution, in a solution without liposomes; 200 mV s⁻¹; (—) first scan, (---) fifteenth scan.

It appears that, at least in our solvent systems and in contrast to that reported for heptylviologen-containing liposomes,² voltammetry in liposome solutions is accompanied by significant phospholipid adsorption. Despite this complication, our systems seem to be convenient means of preparing electroactive, amphiphilic assemblies on electrode surfaces. We are presently exploring the scope of this method and the properties of the quinone films.

We thank the Purdue Research Foundation for financial support.

Received, 13th November 1989; Com. 9/04856A

References

- 1 J. H. Fendler, 'Membrane Mimetic Chemistry,' Wiley, New York, 1982.
 - 2 A. E. Kaifer, *J. Am. Chem. Soc.*, 1986, **108**, 6837.
 - 3 (a) C. J. Miller and M. M. Majda, *J. Am. Chem. Soc.*, 1986, **108**, 3118; (b) J. S. Facci, P. A. Falcigno, and J. M. Gold, *Langmuir*, 1986, **2**, 732; (c) Y. Okahata, G. Enna, K. Taguchi, and T. Seki, *J. Am. Chem. Soc.*, 1985, **107**, 5300; (d) R. D. Mariani and H. D. Abruna, *Electrochim. Acta*, 1987, **32**, 319; (e) J. C. Jernigan, K. O. Wilbourn, and R. W. Murray, *J. Electroanal. Chem.*, 1987, **222**, 193; (f) J. F. Rusling, *Trends Anal. Chem.*, 1988, **7**, 266; (g) C. E. D. Chidsey, C. Bertozzi, and S. H. Glarum, 175th Meeting of the Electrochemical Society, May, 1989, abstract no. 509.
 - 4 (a) C. R. Leidner and M. D. Liu, *J. Am. Chem. Soc.*, 1989, **111**, 6859; (b) C. R. Leidner, H. O'N. Simpson, M. D. Liu, K. M. Horvath, B. E. Howell, and S. J. Dolina, *Tetrahedron Lett.*, 1990, 189.
 - 5 J.-H. Fuhrhop, H. Bartsch, and D. Fritsch, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 804; P. Tundo, D. J. Kippenberger, M. J. Politi, P. Klahn, and J. H. Fendler, *J. Am. Chem. Soc.*, 1982, **104**, 5352; I. Tabushi, I. Hamachi, and Y. Kobuke, *Tetrahedron Lett.*, 1987, **28**, 5899.
 - 6 F. M. Harold, 'The Vital Force: A Study of Bioenergetics,' Freeman, New York, 1986.
 - 7 V. K. Gater, M. D. Love, M. D. Liu, and C. R. Leidner, *J. Electroanal. Chem.*, 1987, **235**, 381; 1988, **257**, 133; K. K. Kasem, W. K. Fife, M. Zeldin, and C. R. Leidner, *ibid.*, submitted.
 - 8 A. J. Bard and L. R. Faulkner, 'Electrochemical Methods,' Wiley, New York, 1980.
 - 9 C. Huang and J. T. Mason, *Proc. Nat. Acad. Sci. USA*, 1978, **75**, 308.
-