

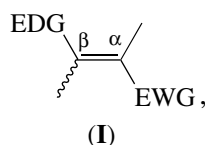
COLLOID CHEMISTRY
AND ELECTROCHEMISTRYElectrochemical Behavior of 5-Substituted
2-Alkylidene-4-Oxothiazolidine Derivatives Studied
by Cyclic Voltammetry¹D. M. Minić^{a, b}, I. Cekić^{a, b}, F. T. Pastor^{b, d}, V. Jovanović^c, and R. Marković^{b, d}^a Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12, Belgrade, Serbia^b Center for Chemistry ICTM, P.O. Box 473, 11001 Belgrade, Serbia^c ICTM, Department of Electrochemistry, P.O. Box 815, 11000 Belgrade, Serbia^d Faculty of Chemistry, University of Belgrade, Studentski trg 16, 11001 Belgrade, Serbia

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Abstract—This study demonstrates the electrochemical activity of selected 2-alkylidene-4-oxothiazolidine compounds containing different substituents at the C5-position on the Pt-electrode in 0.1 M TBAHFP + MeCN in the potential range from –2 V to 2 V. The mechanism of electrode processes is discussed. It is shown that a chemical step is involved in irreversible electrochemical processes. The effect of the substituent at the C5-position on reduction and oxidation potentials is also noted. The regions of a linear dependence of the current peak on the concentration of the compounds examined are determined.

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During our studies focused on the synthesis of stereodefined *push-pull* 2-alkylidene-4-oxothiazolidines [1]

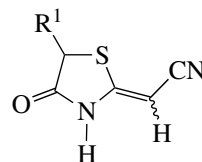



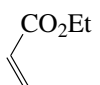
we have been interested in the assessment of the specific physicochemical effects on the reactivity and functionalization [2, 3] of these heterocyclic compounds. Compounds of this type are in the class of push–pull alkenes, containing electron-donating group(s) (EDG) on C(β) and strong resonatively electron-withdrawing group(s) (EWG) on C(α).

Thus, based on the n, π -donor/acceptor properties of 2-alkylidene-4-oxothiazolidines **I** with different electron-withdrawing groups at the terminus of the C=C bond and two electron-donating groups (NH and –S–) at the other terminus, they undergo the well-defined *Z/E*-process, controlled by intra- and intermolecular hydrogen-bond interactions [4–7]. In addition, one of the important structural features of compounds **1** (EWG = COPh, COOEt, etc.) related to the rather close distance between the sulfur and oxygen atoms within the *cis*-configured –S–C=C–C=O moiety can be accounted for by the easy rearrangement of 4-oxothiazolidine to 1,2-dithiole (Scheme, path *E*) [8].

It is interesting to note that 4-oxothiazolidines **1** undergo various oxidation and reduction transformations (Scheme, paths *B* and *F*, respectively). For this

reason and also in view of the broad range of biological activity of thiazolidine derivatives [9] and the intrinsic physicochemical properties of the compounds exemplified by the specific structures **1a–1c**



(R¹ = Me (**1a**),  (**1b**) and  (**1c**)), there

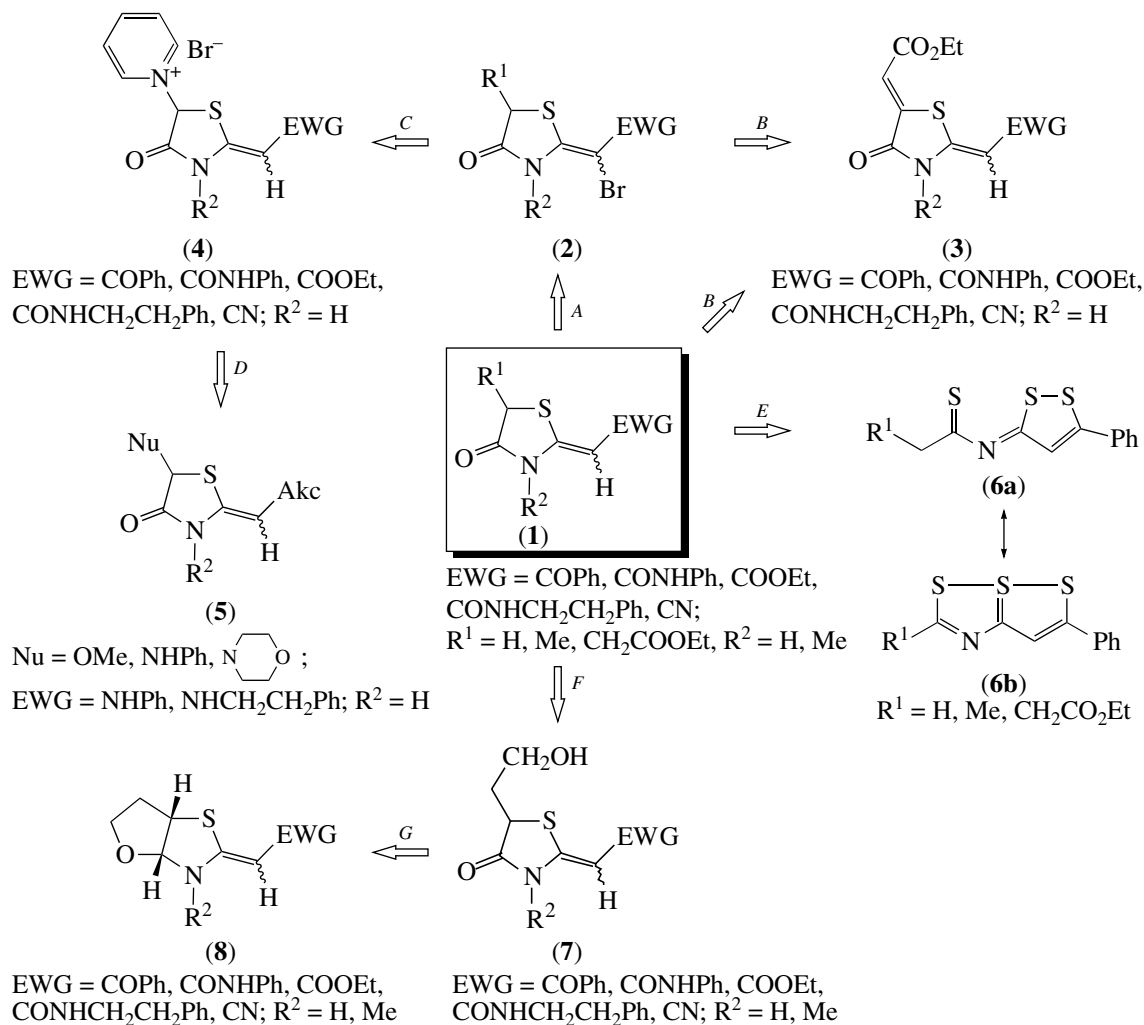
exists a need for electrochemical investigation of these redox processes.

EXPERIMENTAL

Reagents and solutions. Push–pull compounds **1a–1c** were synthesized and characterized in our laboratory according to the procedure described in [1]. All the other reagents employed were of analytical grade. Anhydrous acetonitrile used as a solvent was distilled prior to use. The solutions used in cyclic voltammetry experiments were prepared by dissolving measured amounts of compounds in a 0.1 M solution of TBAHFP in acetonitrile.

Apparatus. Cyclic voltammetry was performed with an Electrochemistry workstation CHI760b (CHI Instruments Co., USA) using a one-compartment electrolytic cell (volumetric capacity 10 ml) with a three-electrode

¹The text was submitted by the authors in English.



Scheme.

configuration. A platinum disc (2.0 mm diameter, CHI Instruments, Inc.) and a platinum flag wire were used as the working and counter electrode, respectively. A silver wire in a 0.01 M AgNO₃ solution of TBAHFP in acetonitrile (anhydrous) served as a nonaqueous reference electrode which was separated from the test solution by a fine glass frit. All the measurements were carried out at room temperature at sweep rates ranging

from 25 to 500 mV/s in the potential range from -2 to 2 V.

RESULTS AND DISCUSSION

The electrochemical properties of compounds **1a**–**1c** at room temperature were investigated by the cyclic voltammetry method in acetonitrile containing 0.1 M

Table 1. Anodic (Ia, IIa) and cathodic (Ic, IIc) peak potentials (V) and peak currents (A) at different sweep rates for the compound **1b**

| Peak | $\nu = 0.05$ V/s | | $\nu = 0.1$ V/s | | $\nu = 0.5$ V/s | |
|------|-------------------|---------|-------------------|---------|-------------------|---------|
| | $i_p \times 10^5$ | E_p | $i_p \times 10^5$ | E_p | $i_p \times 10^5$ | E_p |
| Ic | 3.1250 | -1.1424 | 3.828 | -1.1685 | 8.7550 | -1.2864 |
| Ia | 0.6880 | 0.4848 | 1.5540 | 0.4917 | 5.3820 | 0.5440 |
| IIa | 5.5000 | 1.6224 | 7.3220 | 1.6485 | 14.9700 | 1.7397 |
| IIc | 0.3747 | -0.1227 | 0.9111 | -0.1360 | 2.0370 | -0.2080 |

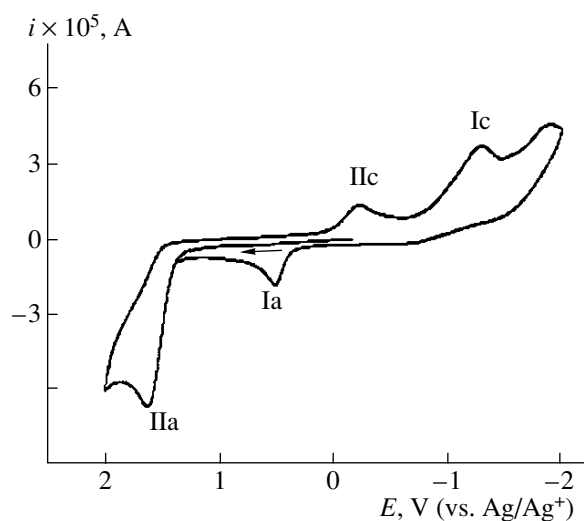


Fig. 1. Cyclic voltammogram of compound **1b**, sweep rate 100 mV/s, concentration 4 mM.

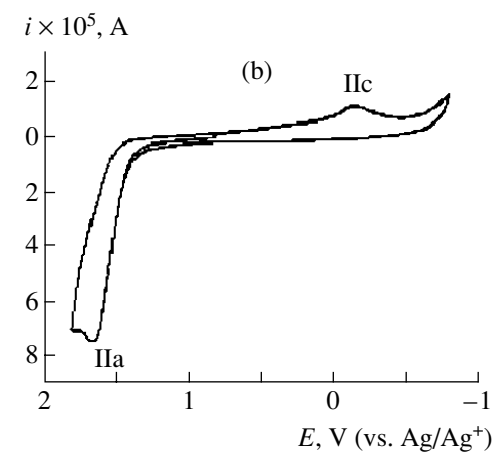
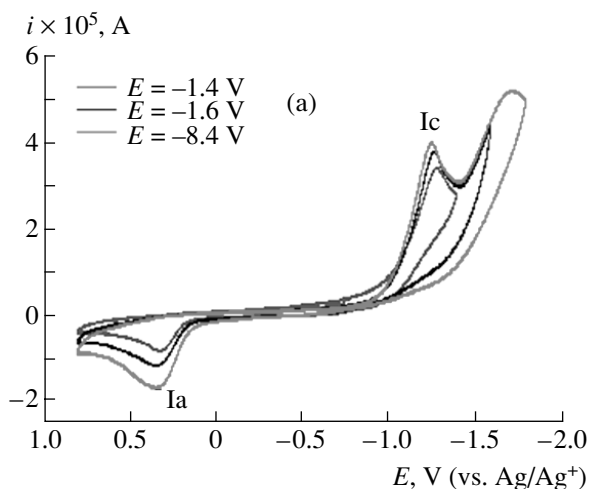


Fig. 2. Cyclic voltammograms of compound **1b**, sweep rate 100 mV/s, concentration 4 mM, cathodic (a) and anodic (b) potential range.

TBAHFP as a supporting electrolyte. Based on the first scan of the cyclic voltammogram of a 4-mM solution of 4-oxothiazolidine **1b** (Fig. 1) and the potential values given in Table 1, this compound, depending on the direction of the applied polarization potential, undergoes irreversible processes of oxidation or reduction on the Pt electrode.

Consequently, as shown in Fig. 2, different electrochemical processes were identified on the basis of the cyclic voltammograms recorded by changing the direction and values of the polarization potential.

According to the theory of cyclic voltammetry, the potential increment between the peak E_p and the half-peak $E_{p/2}$ is given by the expression

$$E_p - E_{p/2}, \text{ V} = 0.048/\alpha n_a,$$

where α is the transfer coefficient and n_a is the number of electrons involved in the rate-determining step. The values of the potential peak differences and αn_a for all compounds **1a–1c** (Table 2) show that the electrode processes are very slow. With an increase in the sweep rate, the differences of the corresponding potential peaks increase and the ratio of the corresponding current peaks decreases. These facts indicate an enhancement of the irreversibility of the processes. The values determined for αn_a imply that the transfer of one electron at the first step of the electrode processes is the rate-determining step [10].

The relatively high values for cathodic and anodic potential peaks, as shown for **1b** (Table 1, columns 3, 5, and 7), indicate an increased stability of the intermolecularly hydrogen-bonded *Z*- and *E*-isomers of thiazolidine compounds **1a–1c**. In addition, the stability of **1a–1c** is attributed to hydrogen bonding interactions

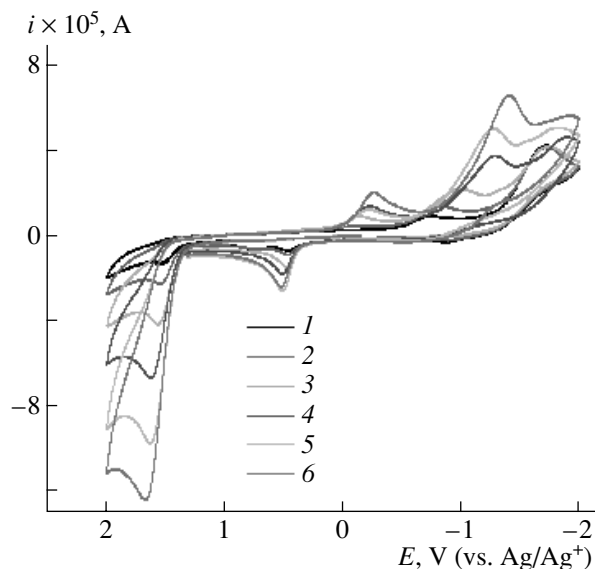


Fig. 3. Cyclic voltammograms for different concentrations (1—0.5, 2—1, 3—2, 4—4, 5—6, 6—8 mM) of compound **1b**, sweep rate 100 mV/s.

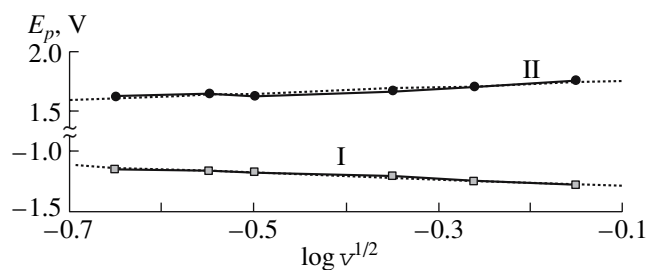


Fig. 4. The plots of E_p vs. $\log v^{1/2}$ for 4 mM concentration of compound **1b**; I—cathodic peak, II—anodic peak.

with relatively polar acetonitrile. This, in turn, is the reason for the rather slow electrode processes. It should be pointed out that the potential peak shifts to more anodic and less cathodic values when the initial concentration of 4-oxothiazolidines **1a–1c** decreases (Fig. 3). Thus, it can be assumed that some chemical reaction can be coupled to the charge-transfer step on the Pt electrode.

The nature of the electrode processes was analyzed in terms of the variations of the potential peak E_p and current peak i_p with sweep rate v by plotting E_p vs $\log v^{1/2}$, $i_p/v^{1/2}c$ vs $v^{1/2}$, and i_p vs v for different concentrations of the thiazolidine derivative **1c** (Figs. 4 and 5).

The E_p values are functions of the polarization rate and vary linearly with $\log v^{1/2}$ (Fig. 4). The current function $i_p/v^{1/2}c$ decreases with $v^{1/2}$ in a way that is strongly dependent on the initial concentration, as shown in Fig. 5. The latter fact leads to the conclusion that the above-mentioned chemical reaction of higher than first-order kinetics is involved in electrochemical processes. Significant influence of the chemical step involved in electroreduction can be observed from the shape of the dependence $i_p/v^{1/2}c$ vs. $v^{1/2}$ for different concentrations (Fig. 5). By taking into account previous studies on electrooxidation of the related compounds [11] and the fact that the dependence of i_p vs v is not linear, which excludes adsorption, we think that the formation of the dimer of the parent compound is involved in the electrode processes.

The number of electrons of the anodic process was determined by the controlled-potential coulometry. The coulometry was performed at +1.6 V for a 10^{-3} M acetonitrile solution of compound **1b**. The electrolysis was

Table 2. The potential increment between the peak E_p and the half-peak $E_{p/2}$ and αn_a

| Compound | Δ_1, V | αn_a | Δ_2, V | αn_a |
|-----------|---------------|--------------|---------------|--------------|
| 1a | 0.188 | 0.25 | 0.163 | 0.29 |
| 1b | 0.221 | 0.22 | 0.141 | 0.34 |
| 1c | 0.096 | 0.50 | 0.088 | 0.54 |

Note: $\Delta_1 = |E_p - E_{p/2}|_{1c}$, $\Delta_2 = |E_p - E_{p/2}|_{11a}$.

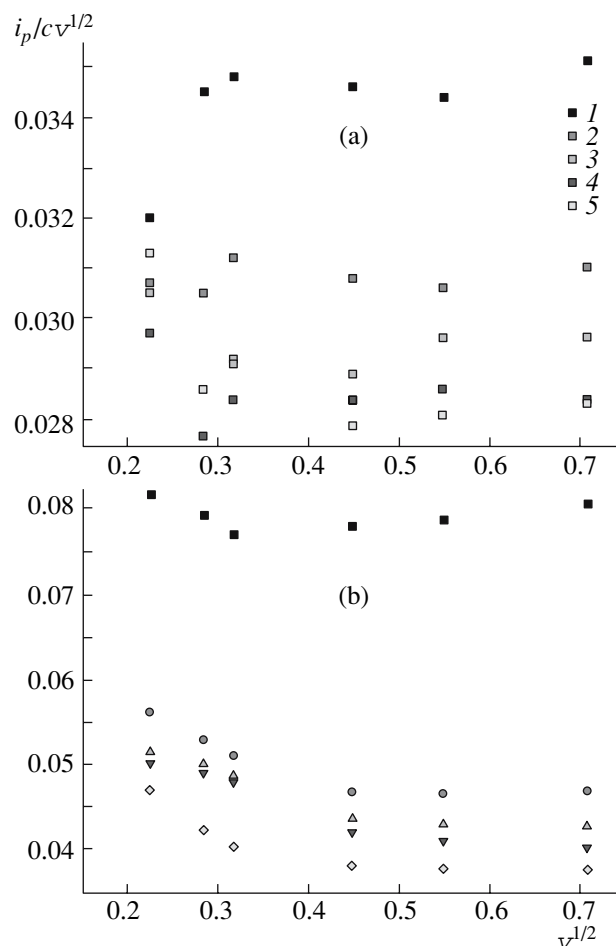


Fig. 5. The plotting $i_p/v^{1/2}c$ vs. $v^{1/2}$ of cathodic I (a) and anodic II (b) peaks for compound **1c**; $c = 1$ (1), 2 (2), 3 (3), 4 (4), and 5 mM (5).

stopped upon current reduction to about 3% of the initial value. The charge passed was 2.21 C and the calculated charge was 1.94 C, assuming that $n = 2$.

It is worth mentioning that the influence of the substituents at the C5-position in the heterocyclic ring regarding the processes of the electrochemical reduction and oxidation was investigated (Fig. 6, Table 3). The cyclic voltammograms of **1a–1c** shown in Fig. 6 indicate a certain regularity in the reduction potentials with respect to the substituent at the C5-position. The

Table 3. The peak potentials (V) of compounds **1a–1c** (versus Ag/Ag⁺)

| Compound | Cathodic peaks | | Anodic peaks | |
|-----------|----------------|-------|--------------|------|
| | I | II | I | II |
| 1a | -1.36 | -0.24 | 0.49 | 1.69 |
| 1b | -1.17 | -0.14 | 0.49 | 1.65 |
| 1c | -1.01 | – | 0.65 | 1.82 |

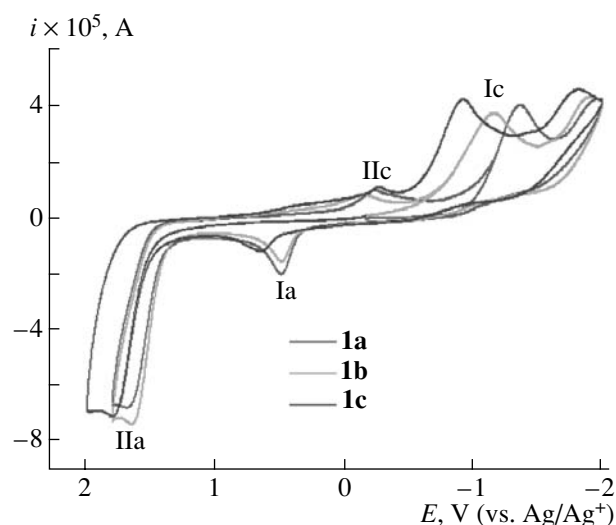


Fig. 6. Cyclic voltammograms of compounds **1a**, **1b**, and **1c** in 0.1 M TBAHFP + CH₃CN, sweep rate 100 mV/s.

order of the reduction potentials of the 4-oxithiazolidines **1a–1c** is as follows: **1a** > **1b** > **1c**.

The rationale for this behavior is most likely based on the increased electron-accepting ability of the etoxycarbonylmethylidene group at C5 of **1c** versus that of the etoxycarbonylmethyl group in **1b**. In the case of precursor **1a** containing the methyl group at C5, a different mode of reduction occurs, thus making the precursor **1c** less reactive. On the other hand, the order of the oxidation potentials follows the opposite direction.

We also tested the possibility of employing this technique for quantitative determination of the heterocyclic derivatives **1a–1c** following the relationship between the current peak and substrate concentration (Fig. 7). As can be seen, the concentration effect on the voltammetric signal follows a linear relationship. This linear relationship, found for low concentrations (0.5×10^{-3} – 2×10^{-3} M), opens up the possibility for an analysis of low amounts of the thiazolidines **1a–1c** in a nonaqueous solution.

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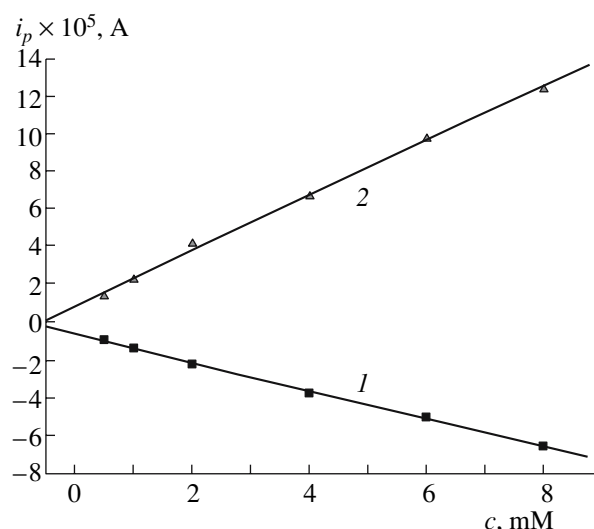


Fig. 7. Dependence of peak current on concentration for compound **1b**; 1; 1—**1c**, 2—**1a**.

REFERENCES

1. R. Marković, Z. Džambaski, and M. Baranac, *Tetrahedron* **57**, 5833 (2001).
2. R. Marković, M. Baranac, P. Steel, et al., *Heterocycles* **65**, 2635 (2005).
3. M. Stojanović, M. Baranac, and R. Marković, *Synlett.*, p. 729 (2006).
4. R. Marković, A. Shirazi, Z. Džambaski, et al., *J. Phys. Org. Chem.* **17**, 118 (2004).
5. H. Kessler, *Angew. Chem., Int. Ed. Engl.* **21**, 512 (1982).
6. J.-C. Zhuo, *Magn. Reson. Chem.* **35**, 311 (1997).
7. J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.* **29**, 1304 (1990).
8. R. Marković, M. Baranac, and S. Jovetić, *Tetrahedron Lett.* **44**, 7087 (2003).
9. R. G. Giles, N. J. Lewis, J. K. Quick, et al., *Tetrahedron* **56**, 4531 (2000).
10. J. O'M. Bockris and A. K. N. Reddy, in *Modern Electrochemistry* (Plenum, New York, 1970), Vol. 2, p. 1081.
11. C. Iwakura, M. Tsunaga, and H. Tamura, *Electrochim. Acta* **17**, 1391 (1972).