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Adsorption of Some Aliphatic Dimercaptans on the Silver Surface Investigated by Raman Spectroscopy

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Adsorption of 1,3-propanedithiol, 1,4-butanedithiol, 1,5-pentanedithiol, and 1,6-hexanedithiol on silver surface has been investigated by surface-enhanced Raman spectroscopy. It has been found that the conformations of the adsorbates were mainly affected by steric interaction of the adsorbates with the surface. As the alkyl chain length separating the thiol groups increased, surface stacking efficiency became increasingly important in determining conformation of the adsorbate on the surface.

Introduction

When a molecule adsorbs on metal surfaces such as Ag, Cu, and Au, its Raman scattering intensity can be tremendously enhanced. This plenomenon, so-called surface-enhanced Raman scattering (SERS)[1-7] has been utilized to obtain vibrational spectra of the adsorbates forming monolayer on the surfaces. The SER spectra thus obtained have proved useful for the investigation of the chemical nature of the adsorbates[8], their orientations with respect to the surface[9-11], and the metal-adsorbate interaction[12,13].

Recently, we have carried out SERS investigation of several aliphatic mercaptans adsorbed on silver surface [11,14-18]. It has been found that these mercaptans adsorbed on the surface dissociatively, namely after losing the thiol protons and that the resulting thiolate anions adsorbed through their sulfur atoms. In addition, the SER spectra provided information on the conformational isomerism of the adsorbed thiolate anions. When the surface was sparsely populated with the adsorbates, various conformational isomers with respect to the C-C bonds adjacent to the sulfur atoms were found. On the other hand, only the trans conformers existed when the adsorbates formed a full monolayer coverage on the surface. This was explained in terms of surface stacking efficiency of the trans conformers.

A similar investigation has been performed on the surface adsorption of 1,2-ethanedithiol. This molecule adsorbed as a bidentate dithiolate dianion after losing two protons. In contrast to the cases of monomercaptans, gauche form was dominant on the surface regardless of surface coverage. This was attributed to less steric interaction of the adsorbed gauche form with the surface than that of the trans form.

In the present paper, the SERS investigation on longer chain dithiols, namely 1,3-propanedithiol (1,3-PDT), 1,4-butanedithiol(1,4-BDT) 1,5-pentanedithiol(1,5-PDT), and 1,6-hexanedithiol(1,6-HDT) is reported. The major purpose of the present work is to investigate further the factors affecting the conformation of the adsorbates.

Experimental

The method of preparation of silver sol and details of Raman scattering measurement have been reported elsewhere[19]. The 514.5 nm line of an Ar⁺ laser(Spectra physics model 164-06) was used as an exciting source. In a typical experiment, the laser power and spectral slit width were 200-300 mW and 5-10cm⁻¹ respectively.

Methanol solutions of dithiols were diluted with water to final concentrations of 10^{-2} M or less. Around $10\,\mu l$ of dithiol solution was injected into 1 m*l* silver sol solution and aqueous polyvinylpyrrolidone (2%, 10-20 μl) was added to stabilize the solution. Dithiolate dianion solutions were prepared by mixing neat dithiols with 3 M NaOH aqueous solution in 1:10 volume rations.

To prepare a silver dithiolate salt, a methanolic solution of 0.5 M dithiol and 1 M silver nitrate solution were mixed in 1:1 volume ratio with vigorous stirring. The yellow precipitate of a silver dithiolate salt was then filtered, and rinsed thoroughly with methanol and water successively. A pellet of silver dithiolate salt was spun at 3000 rpm during the Raman scattering measurment to minimize laser-induced damage.

All the chemicals used were reagent grade and triply

distilled water was used for the preparation of solutions.

Results and Discussion

The ordinary Raman and SER spectra of 1,3-propanedithiol (1,3-PDT), 1,4-butanedithiol(1,4-BDT), 1,5-pentanedithiol(1,5-PDT), and 1,6-hexanedithiol(1,6-HDT) are shown in Figure 1-4, respectively. The SER spectra were recorded at two bulk concentrations, namely at -10^{-6}M and at 10^{-4} M. The reason for recording the SER spectra at different bulk concentrations is to investigate the change in the conformation of an adsorbate with the surface coverage. The ordinary Raman spectra of dithiolate dianions in basic aqueous solutions and of silver dithiolate salts are also shown in the figures. As were the cases for several monomercaptans[11,14-17,20] and 1,2-ethanedithiol[18] investigated previously, dimercaptans(1,3-PDT, 1,4-BDT, 1,5-PDT, and 1,6-HDT) adsorbed on silver surface exhibited strong enhancements of their Raman band intensities. Based on the intensities of the C-S stretching modes appearing in the 600-800 cm^{-1} spectral region, the SER enhancement factors[21] are estimated to be around $2 \times 10^5 - 5 \times 10^5$. Also, as were the cases for mono-and dimercaptans reported previously, the S-H stretching bands at 2558, 2561, 2564, and 2567 cm^{-1} in the ordinary Raman spectra of 1,3-PDT, 1,4-BDT, 1,5-PDT, and 1,6-HDT, respectively, are completely missing in the SER spectra. Peak positions for the C-S stretching bands in the SER spectra are red-shifted by 30-60 cm^{-1} from the corresponding bands in the ordinary Raman spectra. These indicate that the above dimercaptans adsorb dissociatively on the surface after losing two thiol protons and that the dithiolate dianions are bound to the surface via their two sulfur atoms. The same conclusion was drawn on the adsorption mechanism of mercaptans investigated so far.

To investigate the conformation of an adsorbate using Raman spectroscopy, vibrational assignments for each peaks in the spectra are needed. In the cases of monomercaptans[11,14-17] and 1,2-ethanedithiol[18], conformer classifications and vibrational assignments could be carried out utilizing previous assignments reported in the literature and the information available from the SERS works. For the dimercaptans investigated in this work, not much information is available from the literature on the vibrational assignments. Difficulty in the vibrational assignments for these molecules is probably due to the presence of so many conformational isomers and subsequent overlapping of vibrational bands. Instead of attempting complete vibrational assignments for these molecules, conformational isomerism of the adsorbates will be investigated based on general spectral feature, especially the intensities of the C-S stretching bands.

1,3-PDT may exist as a mixture of various rotational isomers related with the conformations around the two C-C bonds and the two C-S bonds. However, Som and Mukherjee[22] have shown that it is necessary to consider the conformation around the two C-C bonds only in the assignment of the vibrational spectra of the molecule in both the solid and neat liquid states. Then, depending on the trans(T) or gauche(G) conformation around each C-C bond, three overall conformations are possible, namely TT, TG, and GG. Som and Mukherjee assigned the bands at 664, 701 and 764 cm^{-1} in Figure 1(a) to the C-S stretching vibrations of GG, GG and TT conformers, respectively. When a SH group is treated as
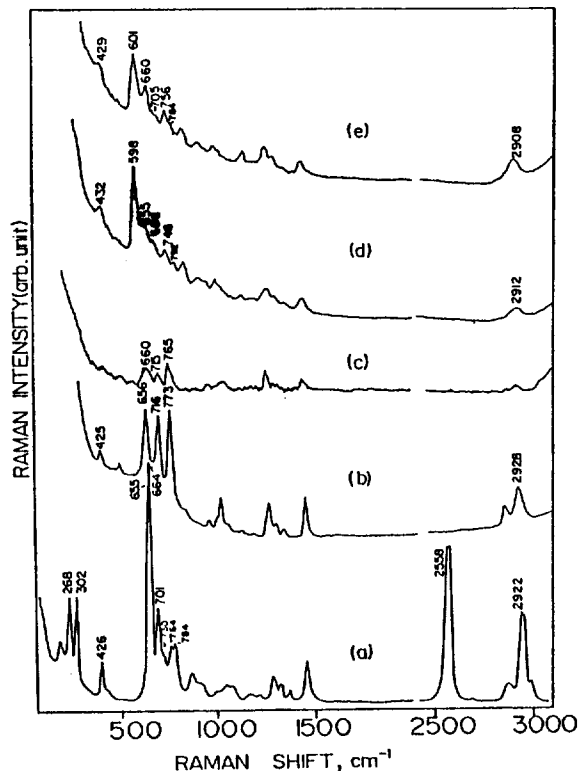
Figure 1. Ordinary Raman spectra of (a) neat 1.3-propanedithiol, (b) aqueous 1,3-propanedithiolate dianion, and (c) silver 1,3-propanedithiolate salt. SER spectra of 1,3-propanedithiol in silver sol at (d) 6×10^{-6} M (e) 10^{-4}M bulk concentrations.

a point mass, molecular geometry of an aliphatic mercaptan should be similar to the corresponding aliphatic chloride. Since both the effective masses and the force constants are much the same for these two groups, the vibrational spectrum of an aliphatic mercaptan is known to be very similar to that of the corresponding halide[23-25]. Thorbjørnsrud et al.[26] and Grindheim and Stølevik[27] observed six bands in the C-Cl stretching region of the infrared and Raman spectra of 1,3-dichloropropane. Two bands at 641 and 678 cm^{-1} were assigned to the GG conformer, two bands at 657 and 727 cm^{-1} to the TG conformer, and two bands at 697 and 784 cm^{-1} to the TT conformer. In the ordinary Raman spectrum (Figure 1(a)) of 1,3-PDT, six bands are observed in the C-S stretching region, namely the bands at 655, 664, 701, 730, 764 and 784 cm^{-1}. It is not certain at all how these bands will correlate with the C-Cl stretching bands for the 1,3-dichloropropane. However, we will correlate these bands with the bands at 641, 657, 678, 697, 727, and 784 cm^{-1}, respectively, appearing in the vibrational spectra of 1,3-dichloropropane. Part of the reason for such correlations is the similarity of the intensity patterns in the same spectral regions of the ordinary Raman spectra of two molecules. Then, the six bands in this region are assigned to the C-S stretching vibrations of 1,3-PDT with GG, TG, GG, TT, TG, and TT conformations, respectively. These assignments are in disagreement with those by Sam and Mukherijee. Especially, the band at 784 cm^{-1} in Figure 1(a) which was assigned to the CH$_2$ rocking mode by Som and Mukherijee is too strong for such an assignment. However, it is possible that this band contains some contribution from a CH$_2$ rocking vibration. Such a view is in complete agreement with

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the assignment of the band at the same position in the vibrational spectra of 1,3-dichloropropane made by Thorbjørnsrud *et al.* According to our previous investigations on aliphatic monomercaptans and 1,2-ethanedithiol, the C-S stretching frequencies shift slightly to red when the thiol protons are lost. In the Raman spectra of silver thiolate salts, the C-S stretching vibrations appear 3-15 cm^{-1} redshifted from the corresponding bands in the Raman spectra of neat thiols. In the Raman spectrum (Figure 1(b)) of aqueous 1,3-propanedithiolate dianions, three bands appear in the C-S stretching region, namely at 656, 716 and 773 cm^{-1}. These bands can be correlated with the bands at 664, 730 and 784 cm^{-1} in Figure 1(a). This implies that only the bands due to TG and TT conformers appear in the Raman spectrum of aqueous dianions. 1,3-Propanedithiolate dianion seems not to exist as a GG conformer probably because the coulombic repulsion between the negative charges destabilize such a conformation. Also, the information from the dianion spectrum provides partial support for the assignments of the C-S stretching vibrations made above. Three broad bands centered at 660, 715 and 765 cm^{-1} appear in the ordinary Raman spectrum (Figure 1(c)) of silver 1,3-propanedithiolate salt. Based on the information from previous investigations on similar compounds described above, these bands can be correlated with the bands at 664, 730 and 784 cm^{-1}. Hence, only the TG and TT conformations of dithiolate are possible in the silver salt also. Five bands appear in the C-S stretching region of the SER spectrum (Figure 1(d)) obtained at low bulk concentration, namely at 598, 655, 698, 748 and 792 cm^{-1}. In the previous SERS investigations of aliphatic monomercaptans and 1,2-ethanedithiol, the C-S stretching frequencies increased by 4-15 cm^{-1} when the bulk concentrations increased such that the surfaces were fully covered with the adsorbates. Correlating the above bands with those at 601, 660, 705, 756 and 784 cm^{-1} in the SER spectrum (Figure 1(e)) obtained at high bulk concentration, it can be concluded that the bands at 598, 655, 698 and 748 cm^{-1} in Figure 1(d) are due to C-S stretching vibrations. On the other hand, the band at 792 cm^{-1} in Figure 1(d) which is red-shifted in Figure 1(e) must not be a C-S stretching vibration. Rather, it may be assigned to a CH_2 rocking mode embedded in the 784 cm^{-1} peak in Figure 1(a). When a mercaptan adsorbs on silver surface, its C-S stretching frequency red-shifts by 20-50 cm^{-1} from the value for neat liquid. Based on this information, the bands at 598, 655, 698 and 748 cm^{-1} in Figure 1(d) can be correlated with the bands at 655, 701, 730 and 784 cm^{-1} in Figure 1(a), respectively. Namely, the first two bands at 598 and 655 cm^{-1} in Figure 1(d) are assigned to the GG conformer while the remaining two at 698 and 748 cm^{-1} are attributed to the TT conformer. Then, since the GG bands are much stronger than the TT bands it can be concluded that the GG conformation of the adsorbate is dominant on the silver surface. The TG conformation which is dominant in neat liquid is hardly present on the surface. Also, by comparing Figure 1(e) with Figure 1(d), it is seen that the GG conformation becomes even more favorable on the surface as the surface coverage increases. This is in complete agreement with the observation made in the previous SERS investigation of 1,2-ethanedithiol. Hence, the steric effect seems to play a major role in determining conformation of adsorbed 1,3-PDT as was the case of 1,2-ethanedithiol.
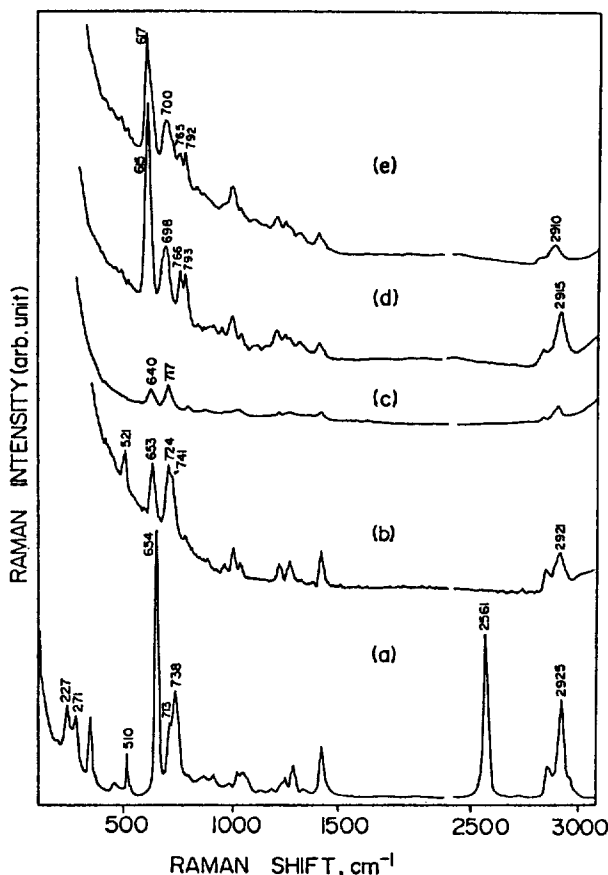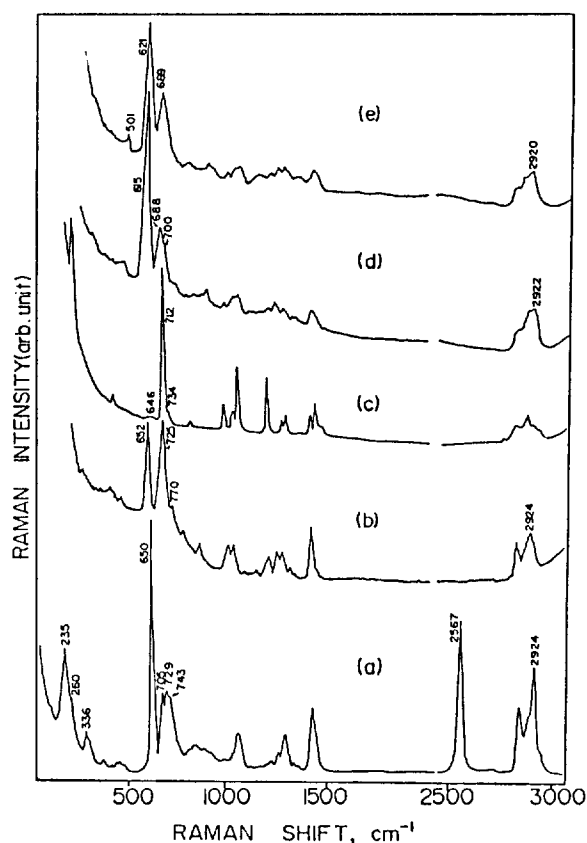

Figure 2. Ordinary Raman spectra of (a) neat 1,4-butanedithiol, (b) aqueous 1,4-butanedithiolate dianion, and (c) silver 1,4-butanedithiolate salt. SER spectra of 1,4-butanedithiol in silver sol at (d) $5 \times 10^{-6} M$ (e) 10^{-4} M bulk concentrations.

No vibrational assignment for 1,4-BDT is available from the literature. For the monomercaptans investigated previously, the C-S stretching vibrations for the gauche and trans conformers with respect to the C-C bonds adjacent to the thiol groups appear at 620-670 cm^{-1} and 710-740 cm^{-1}, respectively. Hence, the band at 654 cm^{-1} and the composite bands at 713 and 738 cm^{-1} in the ordinary Raman spectrum (Figure 2(a)) may be attributed to the gauche and trans conformers in regard to the C-C bonds adjacent to the SH groups. In the ordinary Raman spectrum (Figure 2(c)) of silver 1,4-BDT salt, the corresponding bands appear at 640 and 717 cm^{-1}, respectively. The fact that the latter band is stronger than the former may imply that the trans form is more abundant in this case in contrast to the case of silver 1,3-PDT salt. The corresponding peaks appear at 615 and 698 cm^{-1}, respectively, in the SER spectrum (Figure 2(d)) of 1,4-BDT. Red-shifts of 40 cm^{-1} for each peak upon surface adsorption are in good agreement with the monomercaptan cases. In the case of 1,4-BDT, the trans band at 698 cm^{-1} appears more distinctly in the SER spectrum than in the case of 1,3-PDT indicating that the steric requirement for surface adsorption is less important for 1,4-BDT with long and flexible carbon chain. A supporting evidence for this argument is found in the SER spectrum (Figure 2(e)) recorded at higher surface coverage where the trans-to-gauche intensity ratio is larger than in Figure 2(d).

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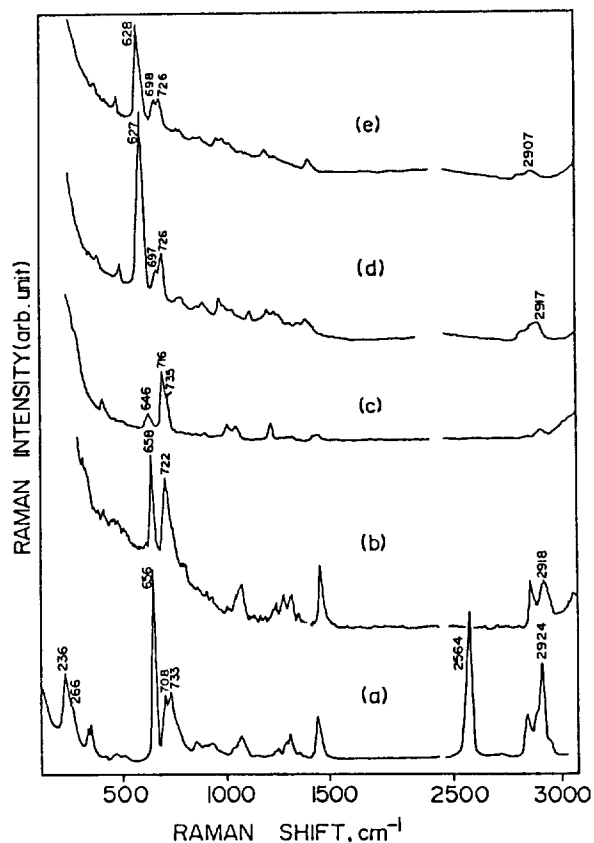
Figure 3. Ordinary Raman spectra of (a) neat 1,5-pentanedithiol, (b) aqueous 1,5-pentanedithiolate dianion, and (c) silver 1,5-pentanedithiolate salt. SER spectra of 1,5-pentanedithiol in silver sol at (d) 5×10^{-6} M (e) 10^{-4} M bulk concentrations.

Figure 4. Ordinary Raman spectra of (a) neat 1,6-hexanedithiol, (b) aqueous 1,6-hexanedithiolate dianion, and (c) silver 1,6-hexanedithiolate salt. SER spectra of 1,6-hexanedithiol in silver sol at (d) 5×10^{-6} M (e) 10^{-4} bulk concentrations.

For 1,5-PDT, the band at 656 cm^{-1} and the composite bands at 708 and 733 cm^{-1} in the ordinary Raman spectrum (Figure 3(a)) can be attributed to the gauche and trans conformers, respectively. These bands may be correlated with the band at 646 cm^{-1} and the composite bands at 716 and 735 cm^{-1}, respectively, in the ordinary Raman spectrum (Figure 3(c)) of the silver salt. It is evident from Figure 3(c) that the trans form is even more dominant in the silver salt of 1,5-PDT. The band at 627 cm^{-1} and the composite bands at 697 and 726 cm^{-1} in the SER spectrum (Figure 3(d)) can be assigned to the C-S stretching vibration of the gauche and trans conformers, respectively. As was the case for 1,4-BDT, the C-S band intensity of the trans conformer relative to that of the gauche form increased with the surface coverage (Figure 3(e)). Similarly, the band at 650 cm^{-1} and the composite bands at 705, 729, and 743 cm^{-1} in the ordinary Raman spectrum (Figure 4(a)) of 1,6-HDT may be attributed to the gauche and trans conformers, respectively. These bands can be correlated with the band at 646 cm^{-1} and the composite bands at 712 and 734 cm^{-1}, respectively, in the ordinary Raman spectrum (Figure 4(c)) of the silver salt. The fact that the latter composite bands dominate in the salt spectrum indicates that the conformations around the C-C bonds adjacent to sulfur atoms are mostly trans. However, in the SER spectrum (Figure 4(d)), the gauche band at 615 cm^{-1} is still stronger than the trans composite bands at 688 and 700 cm^{-1}. The trans composite band intensity increased relative to that

of the gauche band with the surface coverage (Figure 4(e)).

In summary, it has been found that the conformations of adsorbates are determined mostly by the steric interaction of the adsorbates with the surface for all the dimercaptans investigated in the present work. For 1,3-PDT, the steric effect was especially important just as for the case of 1,2-ethanedithiol. However, for the longer chain dithiols, namely 1,4-BDT, 1,5-PDT, and 1,6-HDT, the surface stacking efficiency assumed increasingly important role even though its effect was not as important as for the corresponding silver salts.

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Electrochemical Behaviors of 4-(2-thiazolylazo)-resorcinol in Acetonitrile

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The electrochemical behaviors of 4-(2)-thiazolylazo)-resorcinol (TAR) in acetonitrile solution was studied by DC polarography, cyclic voltammetry, controlled-potential coulometry and UV-V is spectroscopy. The electrochemical reduction of TAR occurs in four-one electron reduction steps in acetonitrile solution. The products of the first and the third electron transfer are speculated to be a relatively stable anion radical. The second electron transfer to the dianion is followed by a chemical reaction producing a protonated species. The product of the fourth electron transfer also produces the corresponding amine compounds with a following reaction. Also every reduction wave was diffusion controlled. The first reduction wave is considerably reversible and the other waves are less reversible.

Introduction

Although the electrochemical reduction of azobenzene and related compounds has been studies extensively[1-6], relatively few studies of the reaction in aprotic media have been reported. Florence[3] reported that azobenzene is reduced via a two-electron electrode reaction to hydrazobenzene in the wide range of pH.

However, if strongly electron-releasing substitutent groups such as –OH or $-NH_2$ are present, the hyrazo derivative is unstable so reduced via a single four electron electrode reaction to amine compound.

Aylward *et al.*[7] reported the polarographic reduction of azobenzene in dimethylformamide (DMF) solution. They proposed that azobenzene is reduced in a rapid one-electron transfer reaction to the anion radical and in a second slow electron transfer to produce a stable dianion.

The aim of this investigation was to study the electroche-

mical reduction of 4-(2-thiazolylazo)-resorcinol(TAR) in acetonitrile(AN) solution using a variety of electrochemical techniques. Then, the polarographic and cyclic voltammetric behavior of TAR in AN solution will be described. The constant potential coulometric reduction of TAR, the analysis of the reduction products, the reversibility of reaction and the type of reduction currents will be given. A mechanism consistent with the experimental results will be proposed.

Experimental

Reagent. 4-(2-thiazolylazo)-resorcinol (TAR) was obtained from Aldrich Co. and was used without further purification. The purification of acetonitrile that was used to solvent based on Coetzee method[8] and tetraethylammonium perchlorate (TEAP) was used as supporting electrolyte was synthesized by Kolthoff method[9].

Polarographic Measurment. Conventional DC polaro-