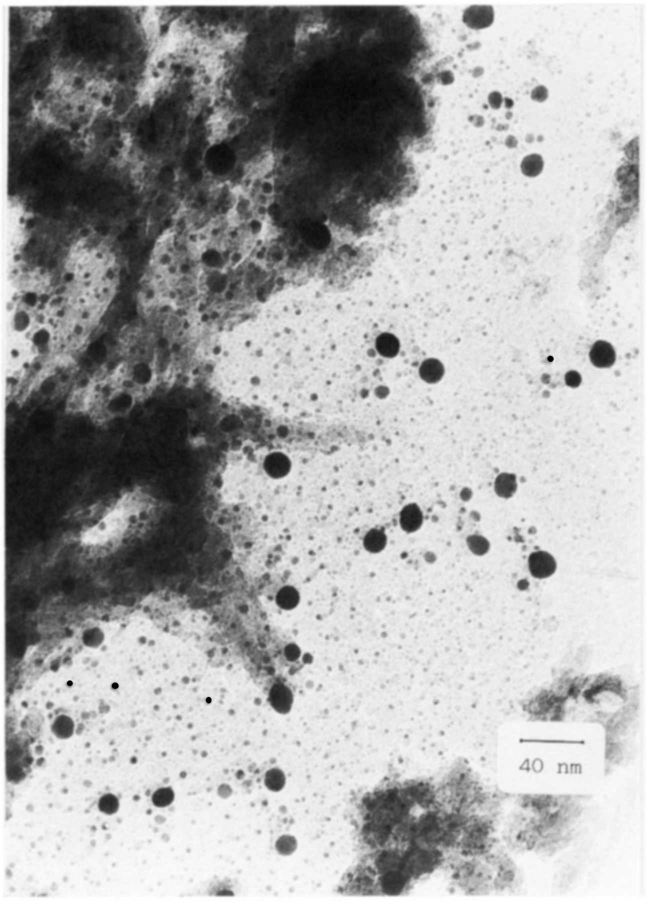

Figure 1. Bright field TEM micrograph of the catalyst.

in order to establish if Pd/XGSILTU and other related systems (obtained by different isocyanates) are able to stereoselectively reduce other selected alkynes.

As expected, TEM investigations carried out on Pd/XGSILTU after some catalytic runs have revealed the presence of nanoscale palladium particles, uniformly dispersed throughout the siloxane matrix. Figure 1 shows that these particles are spheroidal in shape, ranging in size from about 10 to 20 nm. The in situ formation of colloidal metal aggregates, responsible for the hydrogenating activity, does not exclude, however, the persistence of palladium(II) species, possibly protected by a suitable number of thiourea groups. XPS investigations have been planned, in order to clarify this point.

In conclusion, this catalyst exhibits an excellent hydrogenation activity, which is far from being fully exploited. The presence of sulfur donor groups (as in ref 9b) probably prevents the colloidal particles from further aggregation. Furthermore, the new xerogel XGSILTU could play the unprecedented double role of both an efficient recovery agent for palladium(II) from acidic wastes and an effective support for nanoscale palladium particles.

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Registry No. $(EtO)_3Si(CH_2)_3NHC(=S)NHPh$, 42168-35-4; Pd, 7440-05-3; $(EtO)_4Si$, 78-10-4.

Novel Quaternary Salts of Quinoline Oligomer as Metal Surface Protective Materials against Acid Corrosion

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The corrosion of metals at the solid–liquid interface by acids is a problem that is encountered in many industries. One preventive method to subside the corrosion rate of metal in the liquid media is the application of metal surface active organics as corrosion-inhibiting additives in the liquid phase. Some of aromatic heterocyclic organics have been used as corrosion inhibitors under various conditions and applications.[1] However, the use of aromatic heterocyclic polymers as corrosion inhibitors remains rare. They possess promising potential to improve the thermal and chemical stability of materials at elevated temperatures and under highly acidic conditions.

Recently we described a new phenomena of catalytic dehydrogenative polycondensation (CDHP) reaction for the synthesis of linear aromatic heterocyclic oligomers utilizing transition metal sulfides as catalysts as shown in Scheme I.[2–5] The reaction resulted in a catalytic conversion of 1,2,3,4-tetrahydroquinoline (THQ) directly to nonsubstituted quinoline oligomers (**1a** and **1b**)[6] in a one-step synthesis. Here we report that the transformation of these oligomers to their water-soluble quaternary salts makes them suitable for use as metal surface protective agents against acid corrosion.[7]

Due to the electron-accepting properties of oligomer **1**, as demonstrated in its cyclic voltammetry in acetonitrile displaying a reversible one-electron reduction wave with a reductive half-wave potential at −1.78 V vs SCE, the quaternarization reaction of **1** was carried out with reactive alkylation reagents such as dimethyl sulfate or trimethyloxonium salts. Thus oligomeric methylquinolinium methylsulfate **2a** and **2b** (MQO-$MeSO_4$, $x^- = MeSO_4^-$) mixtures were prepared in 80% yield by the reaction of the soluble fraction of corresponding oligomer **1a** and **1b** ($x = 3$–11) with dimethyl sulfate (excess) in dimethyl formamide at 110 °C. The crude products were precipitated from the reaction mixtures by an addition of diethyl ether. The purification process was carried out through a repeated reprecipitation of **2a** and **2b** by an addition of the product solution in a mixture of methanol and H_2O into vigorously stirred acetone. The degree of quaternarization in oligomer **2** was determined by the ^1H NMR spectroscopy. The chemical shift of two groups of methyl protons in DMSO-d_6 centered at 4.51 and 3.32 ppm, corresponding to quinolinium methyl protons and methyl

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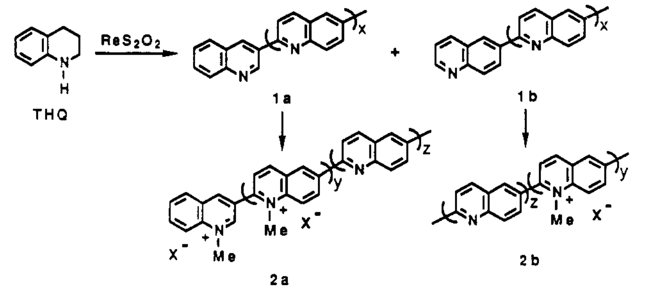
Scheme I



sulfate protons, respectively, can be distinguished easily from the rest of the aromatic protons. The integration ratio between methyl protons and aromatic protons revealed a maximum of 75% quaternarization on quinoline moieties can be achieved. The infrared spectrum (KBr) of **2**: ν_{max} 3445, 3014, 2947, 1598, 1520, 1466, 1352, 1239 (s), 1119, 1059, 1007, 835, 755, 618, and 581 cm^{-1}.

The corrosion inhibition efficiency of oligomeric methylquinolinium methylsulfate in acid media was determined electrochemically by the use of ac impedance spectroscopy.[8-10] The technique involves the measurement of impedance of the corroding interface as a function of frequency. In the experiment, the corroding interface is disturbed from its equilibrium state by the application of a small ac voltage signal whereby an ac current response is obtained. If E is the voltage and I is the current, then the impedance, $Z(\omega)$, which is a function of frequency, is given by eq 1, where E and I are indicated as vector quantities. The polarization resistance, R_p, which is due to the faradaic processes at the interface, can be defined in general by eq 2.

$$Z(\omega) = \tilde{E}/\tilde{I} \qquad (1)$$

$$R_p = Z(\omega \rightarrow 0) - Z(\omega \rightarrow \infty) \qquad (2)$$

In the limit when the frequency, ω, tends to infinity, the impedance becomes equal to R_Ω, the solution resistance. When ω tends to zero, the impedance becomes $R_\Omega + R_p$. According to the correlation developed by Stern and Geary,[11] the reciprocal of the polarization resistance is directly proportional to the rate of corrosion. Therefore, it is sufficient to compare the R_p values between the uninhibited and inhibited experiments to determine the efficiency of given corrosion inhibitor.

A EG&G-PARC ac impedance system was used for the measurement. The electrochemical cell assembly consists of a carbon steel working electrode (the corroding sample), graphite counter electrodes, and a standard calomel reference electrode. A 30% HCl electrolyte solution was used as the corrosive medium with argon bubbling through the electrolyte to keep the acid medium free from oxygen. The measurements were carried out over a range of frequencies and two representative temperatures, 23 and 95 °C.

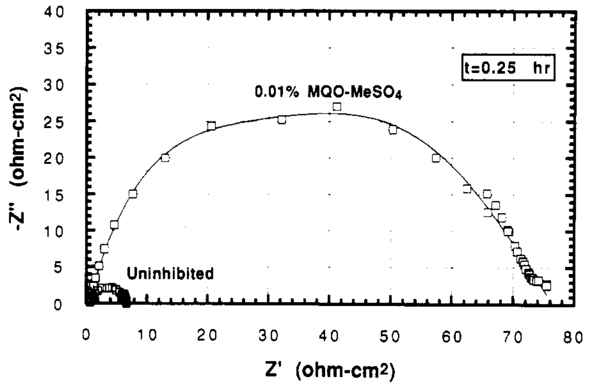


Figure 1. Efficiency of acid corrosion inhibition of oligomeric methylquinolinium methylsulfates (MQO-$MeSO_4$) in terms of the Nyquist plot of impedance data at 23 °C.

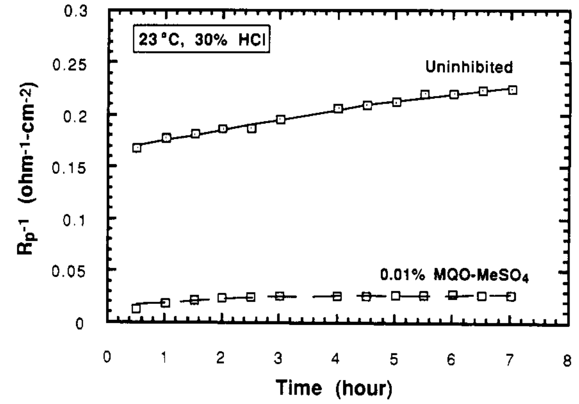


Figure 2. Efficiency of acid corrosion inhibition of oligomeric methylquinolinium methylsulfates (MQO-$MeSO_4$) in terms of polarization resistance of the corroding interface at 23 °C.

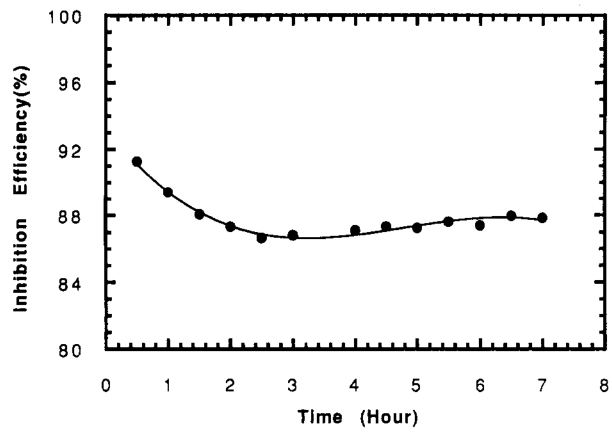


Figure 3. Time dependence of inhibition efficiency of oligomeric methylquinolinium methylsulfates (MQO-$MeSO_4$) at 23 °C.

In the Nyquist representation of impedance results, the imaginary component of the impedance, Z'', is plotted vs the real component, Z', and the different data points represent different frequencies.[12] Normally, a semicircular plot is expected in the ideal case. Results at 23 °C for carbon steel without inhibitor and with 0.01 wt % of oligomeric methylquinolinium methylsulfate (MQO-$MeSO_4$) were compared in Figure 1 for 0.25 h of corrosion. The frequency range used varied from 0.1 Hz to 10 kHz. In the uninhibited case the value of R_p was observed to be 5.95 Ω cm^2 as compared with 72.8 Ω cm^2 for the inhibited case. One can conclude that the corrosion rate, when the inhibitor is used, is a factor of 12 lower than that without using the inhibitor at 0.25 h of corrosion. Similar observations were made at 95 °C. The absolute rates of corrosion, however, were much higher. The R_p value at 0.25 h of corrosion is 0.155 Ω cm^2 for the uninhibited sample as compared with 2.22 Ω cm^2 for the inhibited case. Again, the oligomeric methylquinolinium methylsulfate inhibitor

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suppresses the rate of corrosion by a factor of about 14. The values of the solution resistance, R_{Ω}, were 0.7 Ω cm^2 at 23 °C and 0.1 Ω cm^2 at 95 °C. The time dependence of reciprocal R_p values and values of percent inhibition at 23 °C have been plotted in Figures 2 and 3, respectively. The inhibition efficiency was observed to reach a steady state within 6 h of reaction. The steady-state inhibition efficiency using 0.01% oligomeric methylquinolinium methylsulfate at 23 °C was calculated to be 88%. A similar calculation at a temperature of 95 °C was found to be 90%.

In conclusion, we observed a high anticorrosion efficiency of the quaternary salt of oligoquinolines (**2a** and **2b**) on carbon steel surfaces in aqueous acidic media at both ambient and elevated temperatures. They can be utilized as valuable corrosion inhibitors in the acid-flooding process of oil well exploration. While the exact mechanism of inhibition is unclear, it was hypothesized that positively charged quinoline oligomers being absorbed on the metal surface create an electrostatic field which repels the passage of ferrous ions into solution. If this mechanism is correct, the inhibition action can be extended to other metals.

Registry No. MQO–$MeSO_4$, 138629-29-5; carbon steel, 11121-90-7.

Phase Selectivity in the Simultaneous Synthesis of the T_c = 12.8 K (0.3 kbar) Organic Superconductor κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$ or the Semiconductor $(BEDT\text{-}TTF)Cu[N(CN)_2]_2$

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The discovery of two new radical-cation-based organic superconductors, κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]X$, X = Br ($T_c$ = 11.6 K)[1-3] and Cl (T_c = 12.8 K, 0.3 kbar)[4] possessing new records of high T_c, was reported recently [BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene, or simply ET]. The preparation of single-phase materials is essential for the physical characterization of new organic superconductors. Whereas the Br salt is easily produced as a single-phase material by several different routes,[5,6] two distinctly different phases (rhombic platelets for the superconductor and needles for the second nonsuperconducting phase) were observed simultaneously when the isostructural Cl salt superconductor was prepared. The multiphasic nature of the crystal growth that occurred during the preparation of κ-$(ET)_2Cu[N(CN)_2]Cl$, **1**, was not unprecedented. Whereas the first organic superconductors $[(TMTSF)_2X$, X^- = PF_6^-, AsF_6^-, SbF_6^-, TaF_6^-, ReO_4^-, $ClO_4^-]$[7] were prepared as single-phase materials during the electrocrystallization process, the second class of organic superconducting materials, based on $(ET)_2X$ (X is a monovalent anion), frequently yield multiple crystallographic phases with varying electrical properties.[8] Thus, there often exists a delicate balance of reaction equilibria occurring during electrocrystallization, complicated by the fact that for the preparation of polymeric anions the starting materials frequently do *not* yield the expected anion-containing salts, and these factors must be understood and controlled in order to prepare the desired products.

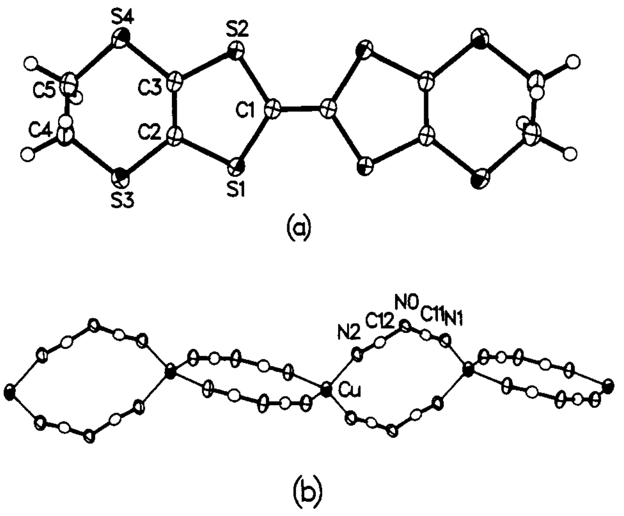

Figure 1. (a) ET molecule with atomic labels. A 2-fold rotation axis perpendicular to the plane of the drawing relates the two halves of the molecule, (b) infinite chain-like polymeric $Cu[N(CN)_2]_2^-$ anion with atomic labels. In both parts of the figure, the atoms (except hydrogen) are drawn with 50% probability ellipsoids, but the scale of (a) is different from that of part (b).

Superconducting κ-$(ET)_2Cu[N(CN)_2]Cl$, **1**, was initially prepared from the electrocrystallization of the ET donor molecule in the presence of CuCl and $PPh_4[N(CN)_2]$.[4] Crystals of the rhombic shaped Cl salt, **1**, are usually smaller than those of the isostructural Br salt grown under identical conditions, and in addition, a second competing needle-shaped product frequently grows simultaneously. In this communication, we report the first characterization of the needle phase, $(ET)Cu[N(CN)_2]_2$, **2**, by use of X-ray diffraction, ESR spectroscopy, four-probe conductivity measurements, and the synthetic procedures required for

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