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## Molecular Dynamics Simulation Study of Density Effects on Vibrational Dephasing in Diatomic Molecular Liquid N<sub>2</sub>

Kwang-Jin Oh, Seung-Joon Jeon\*, Eok Kyun Lee†, and Tae Jun Park‡

*Department of Chemistry, Korea University, Seoul 136-701*

*†Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon 305-338*

*\*Department of Chemistry, Dongkuk University, Seoul 100-715*

*Receive August 23, 1993*

Molecular dynamics simulation was carried out to study density effects on vibrational dephasing. Because of difficulty due to large time scale difference between vibrational motion and vibrational relaxation, we adopt adiabatic approximation in which the vibrational motion is assumed to be much faster than translational and rotational motion. As a result, we are able to study vibrational dephasing by simulating motion of rigid molecules. It is shown that the dephasing time is decreased as density increases and the contribution to this result is mainly due to the mean-squared frequency fluctuation.

### Introduction

Vibrational dephasing has attracted considerable experimental and theoretical attention as a probe of a local structure and dynamics of molecular liquid.<sup>1-6</sup> Vibrational dephasing is that phases of vibrational motion become incoherent and random during any type of vibrational relaxation mechanism. Vibrational dephasing is mathematically expressed by a time-correlation function of vibrational coordinates, and its correlation time measures how fast the time-correlation function decays. It has been known from the Wiener-Khinchine theorem in nonequilibrium statistical mechanics that the time-correlation function of any dynamical variable is related through Fourier transform to its power spectral density which is measured spectroscopically. In the case of vibrational dephasing, the Fourier transform of the time correlation function is related to the isotropic Raman line shape  $I(\omega)$ , which is given by<sup>2</sup>

$$I(\omega) = \frac{1}{2\pi} \int dt \langle a(t)a(0) \rangle$$

$$\approx \frac{1}{2\pi} \left( \frac{\partial a}{\partial Q} \right) \int dt \langle Q(t)Q(0) \rangle$$

Explicit calculations of dephasing time of line shape are quite complex because they require precise knowledge of the interaction potential and correct treatment of the many body dynamics. Although there have been a number of theories which have made different approximations and different choices for the interaction potential and treatment of the many body dynamics such as isolated binary collision model<sup>7</sup>, hydrodynamic model<sup>8</sup>, and Schweizer-Chandler model<sup>9</sup>, these models are not always justified nor are their limits of application clearly stated due to various difficulties. For example, the application of isolated binary collision model is complicated by many-body effects in highly compressed liquids. The hydrodynamic model also has difficulties because of the fact that molecules are pictured as a macroscopic body vibrating in a viscoelastic medium. To test these models experimentally, the dependence of vibrational dephasing on pressure or temperature are currently studied by many researchers.<sup>10</sup> They have, however, ambiguities due to interaction potential

which is not well known, in addition to experimental limitations.

Computer simulations with well-defined interaction potential play a very important role in testing approximations involved in theories on which the interpretation of experimental data is based. In addition, they allow one to ask and answer questions not directly accessible to experiment. By simply varying the parameters of the simulation one can study the effect of various contributions to vibrational dephasing and thereby obtain detailed information which is hardly obtained.

Recently Berens and Wilson have succeeded in carrying out such simulations for the infrared 0-1 fundamental of CO in gaseous and liquid argon. Quantum corrections were applied to the calculated classical spectra, giving excellent agreement with experiment.<sup>11,12</sup> The major problem with direct simulations is difference in time scale between the vibrational period and relaxation time in the liquid. The vibrational motion having frequencies about 1000-3000 cm<sup>-1</sup> is much faster than translational and rotational motion, so that a very short time integration time step is required. On the other hand, dephasing time scale typically ranges from 10 psec to 100 psec, so that very long simulation time is required. As a result, the direct simulation of vibrational motion is difficult. These difficulties can be eliminated by using time-dependent perturbation theory and cumulant expansion method.<sup>13</sup> There have been a number of studies on vibrational dephasing by molecular dynamics simulation based on this method.<sup>14-17</sup> However, there have not existed many systematic studies on density effect which are important to elucidate the dynamics of the condensed phase. For this reason, we investigate systematically density effects on vibrational dephasing of the simplest diatomic molecular liquid N<sub>2</sub> using molecular dynamics simulation.

## Theoretical background

We take the total Hamiltonian to be

$$H = H_0 + H_B + V \quad (1)$$

where  $H_0$  is the isolated molecular vibrational Hamiltonian,  $H_B$  the Hamiltonian for heat bath, that is to say, the translational and rotational degrees of freedom which will be treated classically, and  $V$  the coupling Hamiltonian between isolated molecular vibration and heat bath. If we consider only the fundamental 0-1 vibrational transition and use time dependent perturbation theory and cumulant expansion theory, the vibrational coordinate correlation function is given by<sup>13</sup>

$$\langle Q(t)Q(0) \rangle = Q_{10}^2 \exp(-i\omega_0 t) \langle \exp[\int_0^t dt' \Delta\omega(t')] \rangle \quad (2)$$

where  $\omega_0$  is the vibrational frequency of the isolated molecule and

$$\hbar \Delta\omega(t) = V_{11}(t) - V_{00}(t) \quad (3)$$

In this relation,  $\Delta\omega(t)$  is the instantaneous vibrational frequency shift induced by the environment, and  $V_{ii}$  is the unperturbed vibrational matrix element of the coupling Hamiltonian. The time dependence of  $\Delta\omega(t)$  arises from the classical bath dynamics of rigid molecule, and the ensemble ave-

rage is over bath coordinates. On the assumption of the weak coupling limit, which can be applied for liquid nitrogen, the terms of the cumulant expansion of Eq. (2) can be truncated above second order. Then

$$\langle Q(t)Q(0) \rangle = Q_{10}^2 \exp[-i(\omega_0 + \langle \Delta\omega \rangle)t] \exp\left(-\frac{t}{T_2}\right) \quad (4)$$

where  $\langle \Delta\omega \rangle$  is the average frequency shift due to the bath and the dephasing time,  $T_2$ , is given by

$$T_2^{-1} = \int dt \langle \delta\omega(t) \delta\omega(0) \rangle \quad (5)$$

where  $\delta\omega(t)$  is the frequency fluctuation of molecules due to random motion of the heat bath, which is given by  $\Delta\omega(t) - \langle \Delta\omega \rangle$ .  $T_2^{-1}$  can be rewritten

$$T_2^{-1} = \tau_c \langle \delta\omega(0)^2 \rangle \quad (6)$$

where  $\tau_c$  is the correlation time for the frequency fluctuation which is given by

$$\tau_c = \int dt \frac{\langle \delta\omega(t) \delta\omega(0) \rangle}{\langle \delta\omega(0)^2 \rangle} \quad (7)$$

An explicit form for  $\Delta\omega(t)$  can be obtained by expanding  $V$  in the vibrational coordinate of interest as below.

$$\begin{aligned} V = & \sum_i \left( \frac{\partial V}{\partial Q_i} \right)_0 Q_i + \sum_i \left( \frac{\partial^2 V}{\partial Q_i^2} \right)_0 Q_i^2 + \sum_{i,j>i} \left( \frac{\partial^2 V}{\partial Q_i \partial Q_j} \right)_0 Q_i Q_j \\ & + \sum_i F_1^i Q_i + \sum_i F_2^i Q_i^2 + \sum_{i,j>i} F_3^{ij} Q_i Q_j \end{aligned} \quad (8)$$

The first and second terms give dephasing of surrounding effects due to the fluctuations of oscillator frequency with time. The third term is the contribution from resonant transfer. Higher terms in expansion could be included, but the first three terms suffice for the present calculation because higher terms are small enough to be neglected. For the fundamental 0-1 transition,  $\Delta\omega_i(t)$  is then given by

$$\hbar \Delta\omega_i(t) = (Q_{11} - Q_{00})F_1^i(t) + (Q_{11}^2 - Q_{00}^2)F_2^i(t) + Q_{10}^2 \sum_{j \neq i} F_3^{ij}(t) \quad (9)$$

The first term would vanish for a harmonic oscillator but is in fact most important term for an anharmonic oscillator. The vibrational dephasing has thus been expressed in terms of isolated molecular vibrational matrix elements,  $Q_{11}$ ,  $Q_{00}$ ,  $Q_{10}$ , which were derived using quantum mechanical perturbation method elsewhere<sup>13,17</sup> and correlation function of  $F_1(t)$ ,  $F_2(t)$ , and  $F_3(t)$ , which involve only translational and rotational degrees of freedom. Thus that can be obtained from simulations of rigid, nonvibrating molecules.

## Molecular Dynamics Simulation

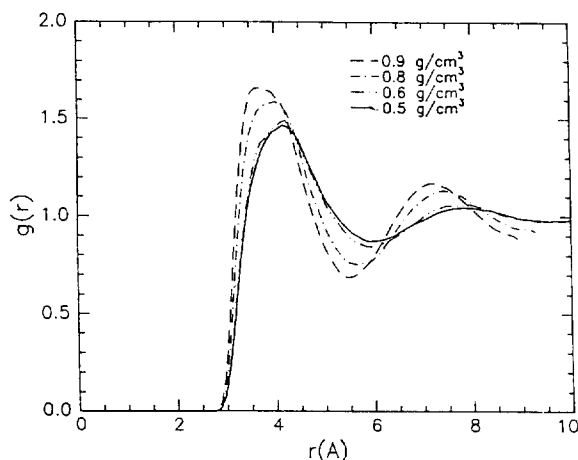
We carried out molecular dynamics simulations of a system with 108 N<sub>2</sub> molecules interacting through 6-12 Lennard-Jones potential with minimum image convention which is given by

$$V(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$

where  $r$  is a distance between interaction sites. We assume that intermolecular interaction can be approximated by sum

**Table 1.** Calculated thermodynamic quantities

| $\rho(\text{g/cm}^3)$ | $T(\text{K})$ | $P(\text{bar})$ | $E(\text{kJ/mol})$ |
|-----------------------|---------------|-----------------|--------------------|
| 0.5                   | 126.0         | 106.0           | -0.32              |
| 0.6                   | 125.2         | 165.5           | -0.88              |
| 0.8                   | 125.9         | 743.8           | -1.94              |
| 0.9                   | 127.6         | 1508.1          | -2.27              |

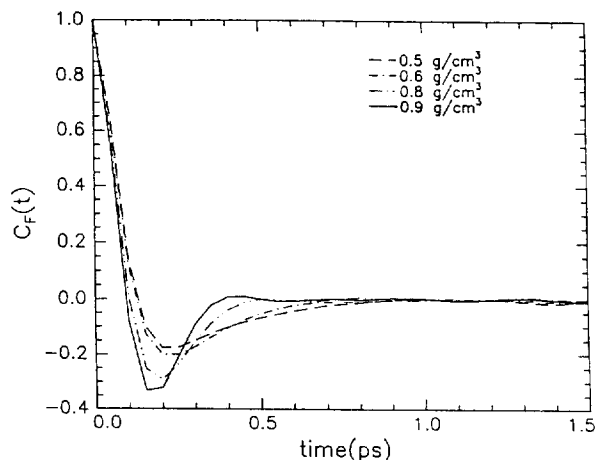
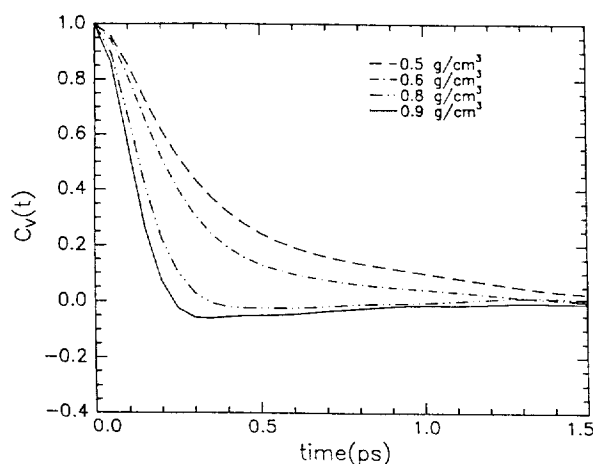
**Figure 1.** Atom-atom pair distribution function of  $N_2$  at various densities.

of site-site interactions. The values of  $\epsilon$  and  $\sigma$  used for this simulation are  $5.151 \times 10^{-22}$  J,  $3.31 \times 10^{-10}$  m, respectively.<sup>13</sup> The equations of motion were integrated by Verlet leap-frog algorithm with 5 femtoseconds of integration time step. The conventional periodic boundary condition were applied to eliminate the finite size effect.<sup>18</sup> The center of mass positions and molecular orientations were generated from  $\alpha$ -FCC lattice sites, and velocities were randomly selected from the Maxwell-Boltzmann distribution. Simulation was initially performed 5000 steps for the system to come to equilibrium while scaling velocities to make a temperature constant. After the system got to equilibrium, further 5000 steps, which correspond to 25 picoseconds, were simulated to calculate various properties. We calculate the normalized autocorrelation function. The internal energy was conserved within about 0.1%.

## Results and Discussion

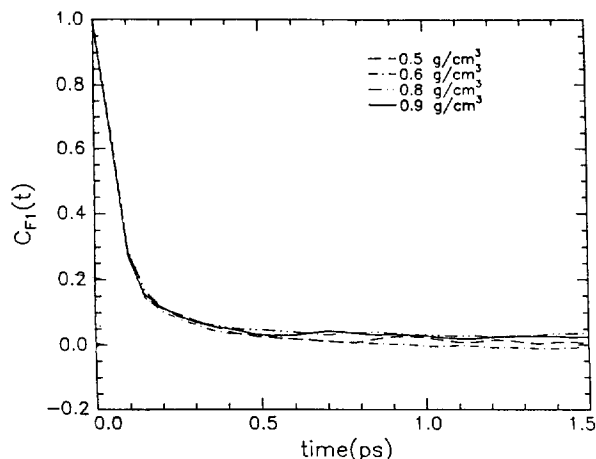
The various calculated thermodynamic quantities are shown in Table 1. The calculated values give good agreement with experimental equation of state of  $N_2$ .<sup>19</sup> Figure 1 shows pair distribution function (PDF) at various densities. As expected, the peaks in PDF sharpen with increasing density, which is typical behavior in liquid.

Figure 2 shows total force autocorrelation function  $C_F(t) = \langle \vec{F}(t) \cdot \vec{F}(0) \rangle / \langle F^2 \rangle$  where  $\vec{F}$  is a total force exerted on the molecular center of mass position. The minimum at around 0.1 ps appears in negative region, which is considered to be occurred due to collisions with neighboring molecules. Since this autocorrelation function is the second derivative of the velocity autocorrelation function, its time integral must va-

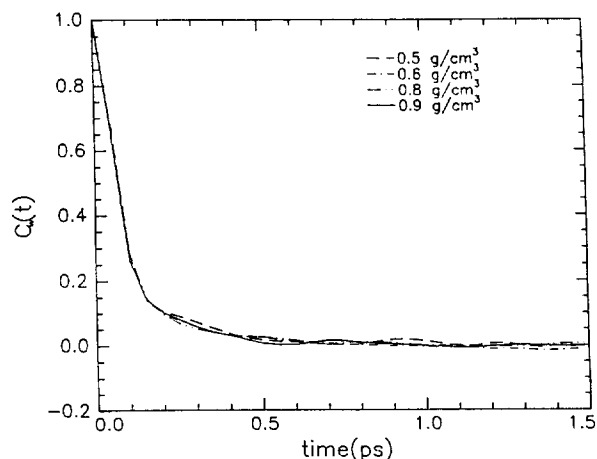
**Figure 2.** Center-of-mass force autocorrelation function of  $N_2$  at various densities.**Figure 3.** Center-of-mass velocity autocorrelation function of  $N_2$  at various densities.

nish with collision, and it therefore shows a negative region. As density increases, the negative minimum moves to more negative and shorter time scale, which means that molecules collide more frequently with neighboring molecules in the highly compressed liquid state. However liquid has more long-range order at higher density as shown in Figure 1. That is to say, molecules in liquid become to have more restriction to move in higher density. Nevertheless, the increase of the collision frequency is inferred to be occurred due to the decrease in average distance between molecules. As a result,  $C_F(t)$  will decay faster in high density than in low density as Figure 2 shows. This similar density dependence also appeared in the center-of-mass velocity autocorrelation function  $C_v(t) = \langle \vec{v} \cdot \vec{v}(0) \rangle / \langle v^2 \rangle$ , which is shown in Figure 3. The time behavior of  $C_v(t)$  is represented by the Taylor series expansion, such as  $C_v(t) = 1 - \langle F^2 \rangle t^2 / 6 m k T + O(t^4)$ . The fact that the mean squared force  $\langle F^2 \rangle$  increases as density increases.

Because  $F_1$ , which is the force exerted on bond axis, is directly related to vibrational dephasing,  $C_{F1}(t) = \langle \vec{F}_1(t) \cdot \vec{F}_1(0) \rangle / \langle F_1^2 \rangle$  was also calculated, and the results at various densities are shown in Figure 4. The time dependences of the various curves are very similar over the whole density range con-



**Figure 4.** Force autocorrelation function along the bond axis of  $N_2$  at various densities.



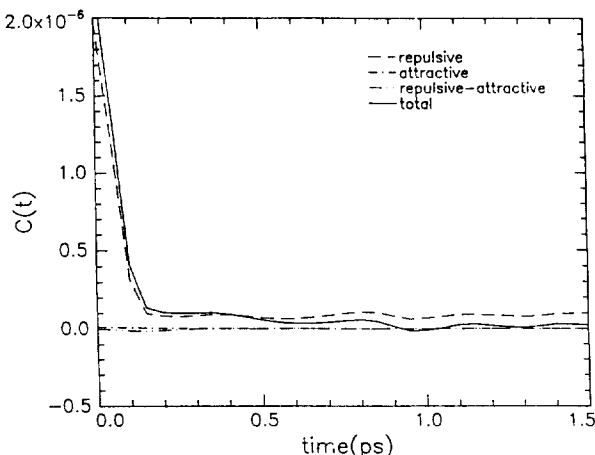
**Figure 5.** Frequency fluctuation autocorrelation function of  $N_2$  at various densities.

dered. The increase of density does not affect the increase of the mean squared force along the bond axis much. It is interesting to note that the minimum does not exist in  $C_{F1}(t)$ , in contrast with  $C_F(t)$ . Therefore, it may be considered that the collisional effect contributes mainly to translation and rotation. The frequency fluctuation autocorrelation functions,  $C_\omega(t) = \langle \delta\omega(t) \cdot \delta\omega(0) \rangle / \langle \delta\omega^2 \rangle$ , at various densities are shown in Figure 5. The shapes of curves at various densities are very similar, as  $C_{F1}(t)$ . It shows that the shape of the normalized frequency fluctuation autocorrelation function  $C_\omega(t)$ , that is to say, the correlation time,  $\tau_c$ , does not vary significantly with density such as  $C_{F1}(t)$ . The correlation time, the mean squared frequency fluctuation, and the dephasing time calculated from equation (6) at various density are given in Table 2. The table shows that the mean squared frequency fluctuation increases, but the correlation time does not change much, as density increases. It is shown from these facts that the decrease of dephasing time with increasing density is mainly due to increase of the mean squared frequency fluctuation as density increases.

Lennard-Jones potential can be divided in two parts by WCA criteria to study the effects of repulsive and attractive

**Table 2.** The correlation time of frequency fluctuation autocorrelation function, the mean squared frequency fluctuation, and pure dephasing time

| $\rho(\text{g/cm}^3)$ | $\tau_c(\text{ps})$ | $\langle \delta\omega^2 \rangle (\text{cm}^{-2})$ | $T_2(\text{ps})$ |
|-----------------------|---------------------|---------------------------------------------------|------------------|
| 0.5                   | 0.110               | 1.46                                              | 174.3            |
| 0.6                   | 0.108               | 1.85                                              | 140.1            |
| 0.8                   | 0.105               | 2.56                                              | 104.2            |
| 0.9                   | 0.105               | 3.61                                              | 73.9             |



**Figure 6.** Various contribution to frequency fluctuation autocorrelation function of  $N_2$  at  $0.7 \text{ g/cm}^3$ .

potential as follows.<sup>18</sup>

$$V(r) = V_r(r) + V_a(r)$$

in which

$$V_r(r) = V(r) + \epsilon(r < r_{\min}), \quad 0 \quad (r_{\min} \leq r)$$

$$V_a(r) = -\epsilon \quad (r < r_{\min}), \quad V(r) \quad (r_{\min} \leq r)$$

where  $r_{\min} = 2^{1/6}\sigma$ . Its individual and crosscorrelation contributions to frequency fluctuation autocorrelation function at the density of  $0.7 \text{ g/cm}^3$  are shown in Figure 6. It is found that the repulsive potential contributes dominantly to total correlation, and the attractive and crosscorrelation effects are negligibly small relative to the repulsive contribution. This results is well-known from previous studies on structural properties such as radial distribution function.<sup>20,21</sup>

Conclusively, the mean squared force fluctuation or frequency fluctuation become larger with increasing density because in higher density liquids have the effect of higher collision frequency, rather than the effect of more long range order. Therefore density effects on vibrational dephasing is mainly dependent on a change of collisional frequency. The collision frequency of Lennard-Jones liquid at higher density is affected by repulsive contribution dominantly. The quantitative comparison with experimental results could not be accomplished, due to lack of experimental results. However this study might be only qualitative. In order for the quantitative interpretation of density effects on vibrational dephasing to be accomplished, more accurate potential should be required.

### Acknowledgement

This work was supported by the Basic Science Research Institute Program, Ministry of Education and Korea Science and Engineering Foundation.

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## Study of Corrosion of Brass Coated Steel Cords in the Acetonitrile Solution of Sulfenamide Derivatives by Tafel Plot and AC Impedance Measurements

Young Chun Ko, Byung Ho Park<sup>†</sup>, Hae Jin Kim<sup>‡</sup>, Q Won Choi<sup>\*</sup>,  
Jongbaik Ree<sup>\*</sup>, and Keun Ho Chung<sup>\*</sup>

Department of Chemistry, Chonnam National University, Kwangju 500-757

<sup>†</sup>Kumho R & D Center, Kwangju 506-040

<sup>‡</sup>Department of Environmental Engineering, Dongshin University, Naju, Chonnam 520-714

<sup>\*</sup>Department of Chemistry, Seoul National University, Seoul 151-742

<sup>\*</sup>Department of Chemistry Education, Chonnam National University, Kwangju 500-757

Received August 24, 1993

Corrosion of brass coated steel cords in the acetonitrile solution of sulfenamide derivatives, *N*-Cyclohexylbenzothiazole-2-sulfenamide (CBTS), *N,N'*-Dicyclohexylbenzothiazole-2-sulfenamide (DCBS), *N*-*tert*-Butylbenzothiazole-2-sulfenamide (TBBS), *N*-*tert*-Amylbenzothiazole-2-sulfenamide (TABS), and *N*-Oxydiethylbenzothiazole-2-sulfenamide (OBTS) was investigated by potentiostatic anodic and cathodic polarization (Tafel plot), DC polarization resistance, and AC impedance measurements. The corrosion current densities and rates are 1.236  $\mu\text{A}/\text{cm}^2$  and 0.655 MPY for CBTS; 1.881  $\mu\text{A}/\text{cm}^2$  and 0.988 MPY for DCBS; 2.367  $\mu\text{A}/\text{cm}^2$  and 1.257 MPY for TBBS; 3.398  $\mu\text{A}/\text{cm}^2$  and 1.809 MPY for TABS, respectively. OBTS among derivatives under study shows the lowest corrosion density (0.546  $\mu\text{A}/\text{cm}^2$ ) and the slowest corrosion rate (0.288 MPY). Also, the charge transfer resistances and the double layer capacitances are 275.21  $\text{k}\Omega\cdot\text{cm}^2$  and 7.0  $\mu\text{F}\cdot\text{cm}^{-2}$  for CBTS; 14.24  $\text{k}\Omega\cdot\text{cm}^2$  and 26  $\mu\text{F}\cdot\text{cm}^{-2}$  for DCBS; 54.15  $\text{k}\Omega\cdot\text{cm}^2$  and 16  $\mu\text{F}\cdot\text{cm}^{-2}$  for TBBS; 0.96  $\text{k}\Omega\cdot\text{cm}^2$  and 83  $\mu\text{F}\cdot\text{cm}^{-2}$  for TABS, respectively. The weaker the electron donating inductive effect of derivatives is and the smaller the effect of steric hindrance is, the more the corrosion of brass coated steel cords in the acetonitrile solution of sulfenamide derivatives is prevented. The above results agree with that observed in the field of tire industry.

### Introduction

In recent years electrochemical techniques for rapid corrosion measurements are increasingly popular among corrosion

workers, because long-term corrosion studies such as traditional weathering tests, weight-loss, and salt spray<sup>1</sup> can require hundreds of hours or even years to detect corrosion with any degree of precision and accuracy, but electrochemi-