

# Notes

## Studies on the Chromatographic Behaviors of Pd(II)- $\alpha$ -isonitroso- $\beta$ -diketone Imine Chelates in Reversed-Phase Liquid Chromatography Using Molecular Descriptors

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In recent year, numerous studies have been conducted to examine the retention mechanism in reversed phase liquid chromatography (RPLC)<sup>1-5</sup> and the solvatochromic comparison method was also used to evaluate the chemical and physical characteristics of a solute that govern retention in RPLC.<sup>6</sup>

Solvatochromism which was described by Sadek and co-workers<sup>6</sup> is a well-established tool of physical organic chemistry that has recently been used to study and correlate factors involved in solvation of ground states, activated complexes, and equilibrium constants of reactions. They first reported the correlation of HPLC retention properties with fundamental dipolarity/polarizability, hydrogen bonding properties of the solutes, and mobile phases. They used solvatochromic parameters and the methodology associated with the linear solvation energy relationships (LSERs) to evaluate the multiple interaction effects that influence HPLC capacity factors.<sup>6,7</sup> Also Cheong and co-workers<sup>8</sup> showed upon examination of the activity coefficients of solutes in mobile phase of various compositions that changes in solute retention in RPLC with mobile phase composition is due mainly to solute-mobile phase interactions. At presents, many studies of retention process in reversed-phase HPLC by the use of the solvatochromic comparison method have been reported continuously.<sup>9-12</sup> While, most of these studies were focused on the elution mechanism of organic compounds such as phenol or benzene derivatives, the retention mechanism of metal chelates have not been investigated.

In our previous study, Lee *et al.* have reported that the elution behavior of Ni(II)- $\alpha$ -isonitroso- $\beta$ -diketone imine chelates in RPLC is affected by the molecular structural parameters of the solutes such as van der Waals volume, polarizability, and dipole moment.<sup>13</sup>

In this work, we have evaluated that the correlation of retention of Pd(II)- $\alpha$ -isonitroso- $\beta$ -diketone imine chelates

with the molecular structural parameters (molecular descriptors) of the chelates. The empirical retention equation was used to evaluate the S index. It was found that the S index for Pd(II) chelates was related to van der Waals volume, polarizability and dipole moments as the molecular descriptors calculated by Gaussian 92 program.

## Experimental

**Instrumentation.** A high performance liquid chromatograph was used a Varian VISTA 5500 equipped with a variable-wavelength UV absorbance detector. A Lichrosorb RP-18 (4.6 mm I.D.×25 cm L, particle size 10  $\mu$ m) column was used and the column was thermostated using universal column heater. Young-in D520A Integrator was used to record chromatograms. Sample injection was performed using a 10  $\mu$ L Hamilton microsyringe.

**Materials.** The  $\alpha$ -isonitroso- $\beta$ -diketone imine and their Pd(II) chelates were prepared by using a modification of the method as described by Lee and Kim.<sup>5</sup> The  $\alpha$ -isonitroso- $\beta$ -diketone imine derivatives as ligand used are listed in Table 1. HPLC-grade methanol and methylene chloride (J. T. Bakers) were filtered with Millipore membrane filter (type FH, pore size 0.45  $\mu$ m), mixed with appropriate volumes of water, then degassed before use. Water was obtained from the Nanopure Deionization system, and was used after filtration with Millipore membrane filter (type HA, pore size 0.45  $\mu$ m). Degassing was accomplished by placing the mobile phase vessel in a ultrasonic bath and applying vacuum for a few minutes. Metal chelate solutions were filtered by using 5  $\mu$ m SEP-PAK (Waters, U. S. A.) syringe filter.

**Liquid chromatographic conditions.** The experimental conditions for the separation of Pd(II) chelates by RPLC were examined with respect to the effect of the flow rate, the type of the sample solvent and the mobile phase composition as summarized in Table 2.

The capacity factor ( $k'$ ) was evaluated using the following equation:

$$k' = (t_R - t_0) / t_0$$

Where  $t_R$  is the solute retention time and  $t_0$  is the column dead time.

Retention data of the Pd(II) chelates were measured as a function of mobile phase composition by varying the vo-

**Table 1.** Abbreviations of  $\alpha$ -isonitroso- $\beta$ -diketone Imine Ligands

| Abbreviation | $\text{R}-\overset{\text{NH}}{\underset{ }{\text{C}}}-\overset{\text{NOH}}{\underset{ }{\text{C}}}-\overset{\text{O}}{\underset{ }{\text{C}}}-\text{R}'$ |                                  |
|--------------|--|----------------------------------|
|              | R  | R'                               |
| H-IMAA-NH    | CH <sub>3</sub>  | OCH <sub>3</sub>                 |
| H-IEAA-NH    | CH <sub>3</sub>  | OCH <sub>2</sub> CH <sub>3</sub> |
| H-IBA-NH     | CH <sub>3</sub>  | C <sub>6</sub> H <sub>5</sub>    |
| H-IDBM-NH    | C <sub>6</sub> H <sub>5</sub>  | C <sub>6</sub> H <sub>5</sub>    |

lume percent of methanol from 66% to 74% at 2% interval.

**Calculation of the Molecular Descriptors of the Pd(II) Chelates.** In order to calculate van der Waals molar volumes, polarizabilities and dipole moments of the Pd(II) chelates, the bond lengths, bond angles and dihedral angles of each metal chelates were first calculated through simulation of three-dimensional structure of the chelates using Chem Draft software. The molecular descriptors of Pd(II) chelates were then calculated by Gaussian 92 program. The STV-3G basis set was used for geometry optimizations. Calculations were performed with SCRf (self-consistent reaction-field) model using the Super-computer at Cornell University.

## Results and Discussion

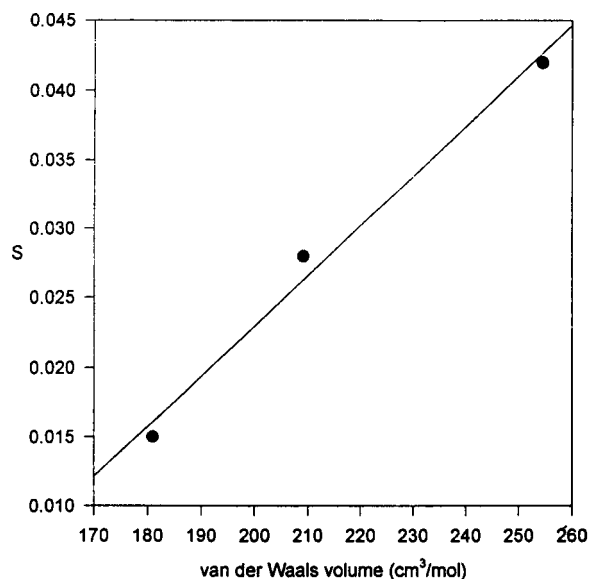
**Table 2.** The Chromatographic Conditions

|                      |  |
|----------------------|--|
| Column               | Lichrosorb RP-18<br>(4 mm I.D.×25 cm L.,<br>particle size 10 μm) |
| Mobile Phase         | Methanol/Water(70/30)  |
| Flow Rate            | 0.9 mL/min.  |
| Solvent of Sample    | Methylene Chloride   |
| Detection Wavelength | 254 nm   |
| AUFS                 | 0.02   |

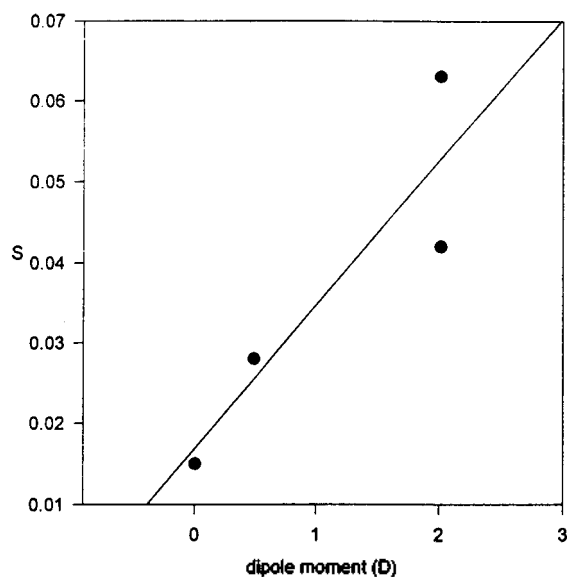
Snyder *et al.*<sup>14-18</sup> have reported that the S index is correlated with some physical properties which are related to the molecular structural parameters of the solute. They showed that there is a tendency for the more polar compounds to exhibit smaller values of S and that the S index quantitatively describes the difference in the free energy change of the solute in a weak and strong solvent. Chen *et al.*<sup>15</sup> also found that S increases as the solute becomes increasingly hydrophobic while it decreases as the solute becomes more hydrophilic. The S index or the hydrophilic index in the empirical retention equation  $\log k' = \log k_w' - S\phi$  is defined as the slope of  $\log k'$  vs. volume fraction of the organic modifier ( $\phi$ ). Where  $\log k_w'$  is the capacity factor obtained by extrapolation of retention data from binary eluents to 100% water. In order to understand the retention mechanism of the Pd(II) chelates in RPLC, we examined the relationship between retention and three molecular structural parameters (molecular descriptors) of the chelates; van der Waals volume, polarizability and dipole moment. The calculated values of these parameters for the Pd(II) chelates are listed in Table 3 along with the S and  $\log k_w'$  values. In this work, the values of  $\log k_w'$  and S for Pd(II) chelates are obtained according to above empirical retention equation. Figure 1 shows that the S values for the Pd(II) chelates are linearly related with their van der Waals volume. This result is in agreement with the observation by Chen *et al.* and indicates that S values increase with solute hydrophobicity.<sup>15</sup> On the other

**Table 3.** Values of S,  $\log k_w'$  and Calculated Molecular Parameters for the Pd(II) Chelates

| Chelates                 | S     | $\log k_w'$ | Molecular Parameters |                |   |
|--------------------------|-------|-------------|----------------------|----------------|---|
|                          |       |             | Dipole Moment (D)    | Polarizability | van der Waals Volume (cm <sup>3</sup> /mol) |
| Pd(IMAA-NH) <sub>2</sub> | 0.015 | 1.184       | 0.003                | 170.794(xx)    | 180.870                                     |
|                          |       |             |                      | -12.340(xy)    |   |
|                          |       |             |                      | 143.039(yy)    |   |
|                          |       |             |                      | 0.000(xz)      |   |
|                          |       |             |                      | 0.000(yz)      |   |
| Pd(IEAA-NH) <sub>2</sub> | 0.028 | 2.302       | 0.485                | 50.667(zz)     | 209.087                                     |
|                          |       |             |                      | 180.538(xx)    |   |
|                          |       |             |                      | -13.267(xy)    |   |
|                          |       |             |                      | 153.154(yy)    |   |
|                          |       |             |                      | 0.002(xz)      |   |
| Pd(IBA-NH) <sub>2</sub>  | 0.042 | 3.474       | 2.017                | -0.005(yz)     | 254.494                                     |
|                          |       |             |                      | 61.278(zz)     |   |
|                          |       |             |                      | 230.516(xx)    |   |
|                          |       |             |                      | -42.702(xy)    |   |
|                          |       |             |                      | 170.176(yy)    |   |
| Pd(IDBM-NH) <sub>2</sub> | 0.063 | 5.375       | 2.021                | -0.041(xz)     | -   |
|                          |       |             |                      | 0.027(yz)      |   |
|                          |       |             |                      | 124.060(zz)    |   |
|                          |       |             |                      | 260.279(xx)    |   |
|                          |       |             |                      | -0.717(xy)     |   |
|                          |       |             |                      | 296.439(yy)    |   |
|                          |       |             |                      | 0.025(xz)      |   |
|                          |       |             |                      | -0.004(yz)     |   |
|                          |       |             |                      | 171.721(zz)    |   |

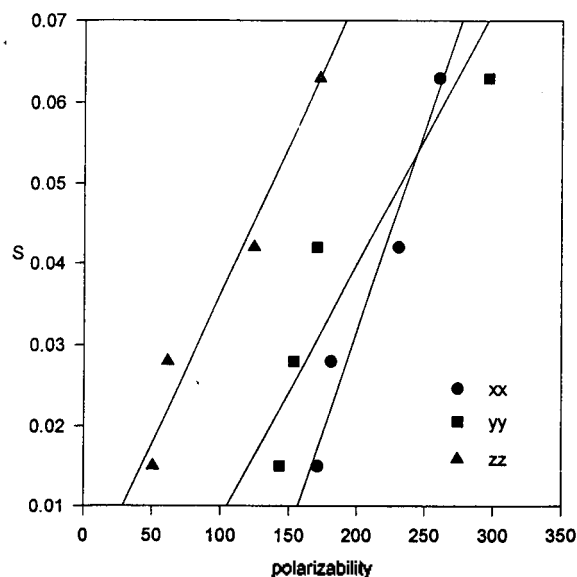


**Figure 1.** Plot of  $S$  vs. van der Waals volume (cm<sup>3</sup>/mol) for Pd(II)- $\alpha$ -isonitroso- $\beta$ -diketone imine chelates in 70/30 methanol/water.

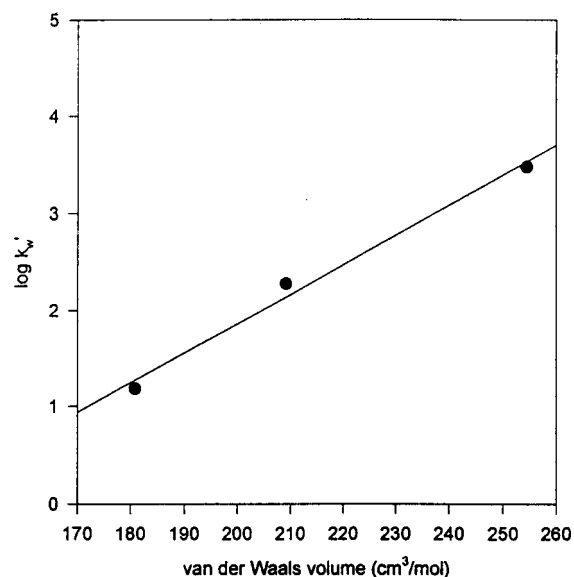


**Figure 2.** Plot of  $S$  vs. dipole moment (D) for Pd(II)- $\alpha$ -isonitroso- $\beta$ -diketone imine chelates in 70/30 methanol/water.

hand, it can be seen in Table 3 and Figure 2 that the  $S$  index increases with increasing dipole moment of the chelate. For most organic solutes the value of the  $S$  index decreases as the polarity of the solutes increases.<sup>15</sup> However, other studies for substituted aromatics showed a clear trend toward larger  $S$  values for molecules with polar and proton donor substituents.<sup>18,19</sup> The ligands in the Pd(II) chelates are polar and possess hydrogen bond acidic NH and NOH groups. Our results are in disagreement with Chen *et al.*,<sup>15</sup> but in agreement with the more recent results by others.<sup>18,19</sup> It seems that the  $S$  values can increase or decrease with dipolarity, depending on the type of the solutes. Linearity is also observed in the plot of  $S$  vs. polarizability as shown



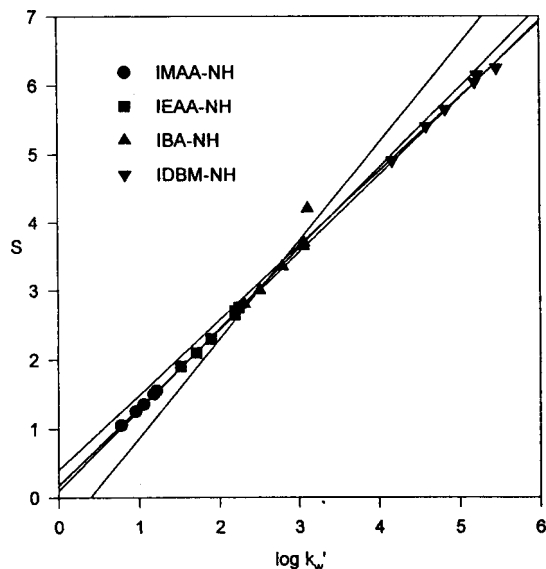
**Figure 3.** Plot of  $S$  vs. polarizability for Pd(II)- $\alpha$ -isonitroso- $\beta$ -diketone imine chelates in 70/30 methanol/water.



**Figure 4.** Plot of  $\log k_r'$  vs. van der Waals volume (cm<sup>3</sup>/mol) for Pd(II)- $\alpha$ -isonitroso- $\beta$ -diketone imine chelates in 70/30 methanol/water.

in Figure 3. Since the polarizability increases with the increase of dipolarity of the chelates, it is thus believed that the values of  $S$  for the Pd(II) chelates studied are affected by both hydrophobic and dipolar properties. Zou *et al.*<sup>18</sup> showed in their correlational study for  $S$  of substituted benzenes with solvatochromic parameters that the most important molecular parameters influencing values of  $S$  are solute molar volume and HB (hydrogen bonding) acidity, with molar volume being the most important parameter. We do not have sufficient number of data points to do a similar correlation work but our results are in agreement with their observation.

When a strong solvent in which the solute dissolves is used, the solute is eluted very quickly from the column.



**Figure 5.** Relationship between  $S$  and  $\log k_w'$  for Pd(II)- $\alpha$ -isonitroso- $\beta$ -diketone imine chelates.

In this case, the forces holding the substance on the stationary phase should be similar to those responsible for dissolution in a solvent. That is, it is the solubility that determines retention and the solubility behavior is explained in terms of molecular interactions.<sup>20</sup> The factors which influence solubility are van der Waals (London dispersion) forces, dipole-dipole, hydrogen bonding, and repulsion forces, etc. In RPLC, the most important factor is a hydrophobic interaction. If the hydrogen bonding and coulombic forces are negligible, the retention of molecules will depend on their size, measured by van der Waals volume. Linear relationship between van der Waals volume and  $\log k_w'$  as shown in Figure 4 and linear relationships between  $S$  and  $\log k_w'$  (Figure 5) for the Pd(II) chelates together indicate that the  $S$  index and retention of the Pd(II) chelates increase with increasing van der Waals volume. This seems to indicate that van der Waals volume is the more contributing factor in determining retention of the Pd(II) chelates in RPLC than dipole moment and polarizability.

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### Theoretical Study of the Frequency-Dependent First- and Third-Order Polarizabilities of Thiophene Oligomers

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Heterocyclic organic systems have attracted particular attention as the materials with large nonlinear optical properties.<sup>1,2</sup> In particular, organic compounds containing heterocyclic moieties (thiophene, pyrrole, furan) are well known to exhibit significant NLO behavior.<sup>3</sup> The nonlinear optical properties of analogs of heterocyclic molecules, such as hetero-(X=O, S, Se, Te)-TCNQ (tetracyanoquinodimethane) and TTF (tetrathiafulvalene) have been investigated.<sup>4,5</sup> Polythiophene is one of the most widely investigated  $\pi$ -conjugated systems representing quasi one-dimensional conductors.<sup>6</sup> In this paper, we present the frequency-dependent first-order polarizabilities,  $\alpha$ , and third-order polarizabilities,  $\gamma$ , for the thiophene oligomers with repeating units  $n=1-13$ . Undoped polythiophene exhibits large third-order nonlinear optical responses.<sup>7-9</sup>

The component in the  $i$ -th molecular fixed-coordinate dire-