

6 α -[1-(R)-Hydroxyethyl]-3-methoxy-7-oxo-1-azabicyclo(3,2,0)-hept-2-ene-2-carboxylic Acid 4. Into the solution of the methyl ester **3** (1g, 4.12 mmol), which was obtained from the hydrogenation of *p*-nitrobenzyl 6 α -[1-(R)-hydroxyethyl]-3-hydroxy-7-oxo-1-azabicyclo(3,2,0)-hept-2-ene-2-carboxylate⁴ followed by treatment with excess of ethereal diazomethane [mass of methyl ester; *m/e*(relative intensity); 241(M⁺,13), 259(M+H₂O⁺,45), 112(100), NMR(CDCl₃) δ : 1.33(d,3H,-CH₃), 2.78(dd,2H,-CH₂-), 2.94(dd,1H,-C₆H), 3.66(s,3H,-OCH₃), 3.70(s,3H,-OCH₃), 3.99-4.25(m,3H,-CHO,-C₅H,-OH)], in 0.05M-phosphate buffer (50 ml) and acetone (3 ml) was added PLE (1.5 ml, suspension of ammonium sulfate buffer) at 25 °C and stirred 2 days in constant adjustment of pH 8.0. Excess of acetone was poured and stirred for 10 min and filtered off any insoluble material. The filtrate was washed with methylene chloride and the water solution was adjusted with HCl to pH = 2.0 and extracted with ethyl acetate. The organic solvent was washed with brine, dried over MgSO₄ and evaporated to give the desired product (147 mg, 15% yield).

Mass *m/e*(relative intensity); 227(M⁺,7), 112(100)
NMR(CDCl₃) δ = 1.10(d,3H,-CH₃), 2.40-2.90(m,3H,-CH₂,C₆H), 3.58(s,3H,-OCH₃), 3.70-4.10(m,3H,C₅H,-CHO,-OH)

7-Aminodeacetylcephalosporanic Acid (7-ADCA) 6. 7-ADCA (1.88g, 0.88mmol) was stirred at room temperature overnight in 5%-H₂SO₄ in anhydrous methanolic solution (100 ml). Water (100 ml) was added and extracted with methylene chloride, dried over MgSO₄, solvent evaporated

to give the desired methyl ester which was pure enough to use for the next hydrolysis reaction. Into the solution of the methyl ester **5** (0.1g, 0.44 mmol) in water (14 ml), 0.1 M-phosphate buffer (4 ml) and acetone (2 ml) was added PLE (0.2 ml, suspension of ammonium sulfate buffer) at 25 °C and stirred overnight in constant adjustment of pH = 8.0. Excess of acetone was poured and stirred for 10 min and filtered off any insoluble material. The filtrate was washed with methylene chloride and the water solution was adjusted with HCl to pH = 2.0 and extracted with ethylacetate. The organic solvent was washed with brine, dried over MgSO₄ and evaporation of the solvent gave the product which was identical to the commercially available 7-ADCA (90 mg, 95% yield).

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A Study of the Parameters of the Retention of Monosubstituted Benzenes in Reversed-Phase Liquid Chromatography

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The relationship between the solute retention and physical parameters describing the interaction between the solute and mobile phase was investigated to predict the solute retention easily in RPLC. The retention data of monosubstituted benzenes were measured on the μ -Bondapak C₁₈ and phenyl columns with methanol-water systems. The linear relationship between dielectric increment(ϵ') and retention data was observed. When the solute form hydrogen bonding with solvent molecules, the slope of the $\ln k'$ vs. ϵ' plot is changed as the compositions is varied. The quadric relationship between mixed solvent solubility parameter (δ_M) and retention data was observed.

Introduction

In recent years, many theories have been reported about the solute retention in reversed-phase liquid chromatography (RPLC)¹⁻³. However, most of them are too complicated to apply for practical purposes and are not easy to predict the retention in several different conditions. Therefore, in this paper we report the results of our study on the relationship between the solute retention and physical parameters des-

cribing the interaction between the solute and mobile phase. This will allow the parameter to be used to predict the solute retention easily in RPLC.

Experimental

Instruments. Waters Associates liquid chromatographic system used consisted of M-440 Absorbance Detector, M-45 Solvent Delivery System, and M-U6K Universal Injec-

tor. Chromatograms were recorded on Bausch and Lomb Omniscribe Recorder. The detection wavelength was 254 nm and the sensitivity was set at 0.05 AUFS. The chart speed was 1.0 cm/min, and the flow rate of mobile phase was 1.0 ml/min.

Standard Solutions. Compounds were first grade or reagent grade chemicals and were purified by simple distillation or recrystallization. Standard solutions were prepared by dissolving the compounds in HPLC grade methanol and then by removing the particles greater than 0.5 μm with Waters Sample Clarification Kit.

Mobile Phases. For mobile phase, HPLC grade methanol and water were mixed by volume ratio. Each mixture was allowed to equilibrate for 1 hr. and then filtered through 0.5 μm Millipore organic filter. The gas bubbles in the solution were removed by vibrating the solution for about 20 min. in an ultrasonic bath.

Stationary Phases. Two columns were used: a 3.9 mm \times 30 cm Waters μ -Bondapak C_{18} column and a 3.9 mm \times 30 cm Waters μ -Bondapak phenyl column.

Measurements. The retention of solute is expressed by capacity factor, k'

$$k' = \frac{t_R - t_0}{t_0}$$

where t_R and t_0 are the retention time of solute and methanol peak, respectively.

Results and Discussion

Two assumptions were made in this study. First, we assumed that solute-mobile phase interaction contributed more to the solute retention than solute-stationary phase interaction did. Therefore, we only considered the interaction between solute and mobile phase. Second, we assumed that the solvent molecule in the vicinity of the solute was different in behavior from that of the bulk solvent molecules.

So far, the parameter, which has been used to predict the solute retention thermodynamically or experimentally, describes bulk properties of solutes or mobile phases. But, it is not appropriate to explain the solute-mobile phase interaction with such bulk properties. Therefore, this study considered the parameter which represent the change in interaction between solute and the solvent molecules adjacent to the solute as the mobile phase changes. The correlations of dielectric increment-solute retention and mixed solvent solubility parameter-solute retention have been examined. The retention data of benzene and substituted benzene at different methanol compositions are shown in Table 1 and 2.

The Effect of Dielectric Increment on Solute Retention. When the polar solutes were added to the solution, the polarization phenomena were used to present the solute-solution interaction. Clausius and Mosotti⁴ expressed the interaction between the external field and the polarization of the individual molecules. Onsagar⁵ considered a molecule in solution as a cavity formed in the medium which has a homogeneous dielectric constant and determined the local field of the molecule.

When small amount of polar solute is added to the solution, the dielectric constant of the solution is given by the Onsagar equation as

where ϵ' is the dielectric increment, ϵ_1 and ϵ_2 are the dielec-

Table 1. Capacity Factor (k') of Monosubstituted Benzenes on μ -Bondapak C_{18} Column in $\text{CH}_3\text{OH-H}_2\text{O}$ System

| Substituted group | % CH_3OH | | | | | | | | |
|------------------------|--------------------------|------|------|------|-------|-------|-------|-------|-------|
| | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 |
| Benzene | 0.68 | 0.98 | 1.86 | 2.38 | 5.00 | 10.15 | 14.52 | 20.77 | 33.70 |
| CH_3 | 0.81 | 1.26 | 2.68 | 4.40 | 10.58 | 21.39 | — | — | — |
| C_2H_5 | 0.91 | 1.41 | 3.78 | 7.10 | 17.60 | — | — | — | — |
| F | 0.63 | 0.93 | 1.93 | 2.81 | 5.71 | 12.42 | — | — | — |
| Cl | 0.80 | 1.26 | 2.78 | 4.54 | 10.00 | 26.77 | — | — | — |
| Br | 0.83 | 1.37 | 2.82 | 5.15 | 12.17 | 31.08 | — | — | — |
| I | 0.89 | 1.52 | 3.45 | 6.50 | 16.00 | 44.58 | — | — | — |
| OH | 0.46 | 0.53 | 0.78 | 0.98 | 1.68 | 3.05 | 4.10 | 6.36 | 10.78 |
| NH_2 | 0.39 | 0.51 | 0.76 | 0.84 | 1.33 | 2.24 | 2.83 | 4.40 | 7.49 |
| CH_2OH | 0.47 | 0.52 | 0.83 | 0.98 | 1.68 | 3.03 | 4.43 | 7.13 | 13.04 |

Table 2. Capacity Factor (k') of Monosubstituted Benzenes on μ -Bondapak Phenyl Column in $\text{CH}_3\text{OH-H}_2\text{O}$ System

| Substituted group | % CH_3OH | | | | | | | | |
|------------------------|--------------------------|------|------|------|------|-------|------|------|------|
| | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 |
| Benzene | 0.13 | 0.26 | 0.51 | 0.87 | 1.65 | 2.97 | — | — | — |
| CH_3 | 0.16 | 0.33 | 0.68 | 1.28 | 2.75 | 5.21 | — | — | — |
| C_2H_5 | 0.18 | 0.39 | 0.88 | 1.84 | 4.44 | 10.28 | — | — | — |
| F | 0.13 | 0.26 | 0.52 | 0.92 | 1.82 | 3.53 | — | — | — |
| Cl | 0.16 | 0.33 | 0.71 | 1.38 | 3.00 | 6.75 | — | — | — |
| Br | 0.18 | 0.39 | 0.79 | 1.57 | 3.60 | 8.50 | — | — | — |
| I | 0.20 | 0.43 | 0.92 | 1.93 | 4.85 | 11.13 | — | — | — |
| OH | 0.07 | 0.14 | 0.25 | 0.39 | 0.86 | 1.27 | 1.82 | 2.23 | 3.16 |
| NH_2 | 0.12 | 0.16 | 0.29 | 0.43 | 0.93 | 1.46 | 1.68 | 2.89 | 4.22 |
| CH_2OH | 0.08 | 0.14 | 0.26 | 0.41 | 0.71 | 1.48 | 1.90 | 2.72 | 3.63 |

$$\epsilon = \epsilon_1 + \left[\frac{(\epsilon_2 - 1)(2\epsilon_2 + 1)}{2\epsilon_2} - (\epsilon_1 - 1) \right] \frac{v_2}{1000} C_2 \quad (1)$$

$$\epsilon' = \left[\frac{(\epsilon_2 - 1)(2\epsilon_2 + 1)}{2\epsilon_2} - (\epsilon_1 - 1) \right] \frac{v_2}{1000} \quad (2)$$

tric constants of solvent and solute, respectively. v_2 is the solute molar volume and C_2 is the solute molarity. The dielectric increment, ϵ' describes the change in dielectric constant occurring between the solute and the surrounding solvent molecules in solution. It is a characteristic value of the solute in the system.⁶

The relationship between the solute retention and the dielectric increment, ϵ' was examined in Figure 1, 2 and 3. The plots have been obtained using the μ -Bondapak C_{18} column as the stationary phase and water-methanol mixtures as the mobile phase by varying composition of methanol from 10 to 90%.

The solutes examined in Figure 1 are phenol, aniline, and benzyl alcohol which form strong hydrogen bonding with methanol-water mixtures. The solute-solvent hydrogen bonding causes big increases in the dipole moment of solute by solvent effect which affects the electron migration.⁷ From electrostatic considerations, the layer of solvent immediately surrounding the solute is made up predominantly of solvent

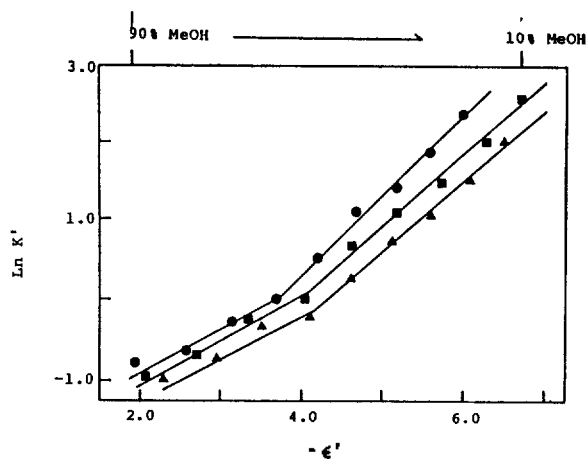


Figure 1. Relationship between dielectric increment ($-\epsilon'$) and $\text{Ln } k'$ values of phenol (●), aniline (▲), and benzyl alcohol (■) on the u-Bondapak C_{18} column.

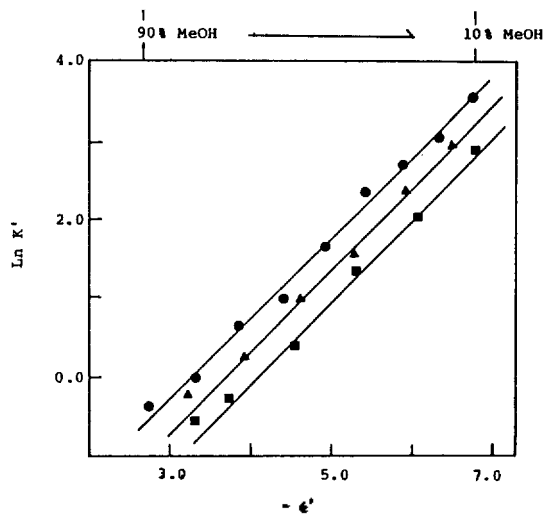


Figure 2. Relationship between dielectric increment ($-\epsilon'$) and $\text{Ln } k'$ values of benzene (●), toluene (▲), and ethylbenzene (■) on the u-Bondapak C_{18} column.

mixture constituent having the higher dielectric constant. Therefore, the shell of solvent constituent of higher dielectric constant serves to act as an electrostatic shield and thus decreases the effective dipole moment of the solute.⁸

When the solutes in Figure 1 form hydrogen bonding with methanol-water mixture, the solutes act as a proton-donor and methanol acts as a proton-acceptor. Thus, an increase in methanol composition in mobile phase leads to stronger hydrogen bondings and a larger dipole moment. Since the dielectric constant of mobile phase becomes smaller as the methanol composition increases, the effect of dielectric constant on the dipole moment will decrease compared to the effect of hydrogen bonding on the dipole moment. Therefore, the effective dipole moment of solute increases. As a result, increased Keesom interaction between the solute and mobile phase decreases solute retention.

However, at compositions less than 60% methanol, the dielectric constant of mobile phase becomes bigger and the hydrogen bonding between solute and mobile phase becomes weaker. As a consequence of shielding effect of bigger dielectric constant of mobile phase, the effective dipole mo-

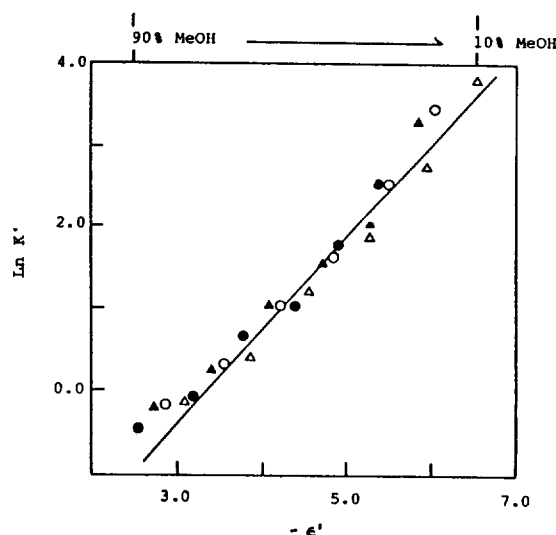


Figure 3. Relationship between dielectric increment ($-\epsilon'$) and $\text{Ln } k'$ values of fluorobenzene (●), chlorobenzene (▲), bromobenzene (○), and iodobenzene (Δ) on the u-Bondapak C_{18} column.

ment of solute will become reduced and a decrease in Keesom interaction will occur. As shown in Figure 1, the rate of increase in retention increases sharply compared to ϵ' above 60% methanol.

The dielectric increment, ϵ' is related to Keesom interaction⁸ by

$$\epsilon' = \frac{9}{2000} \left[20.6 \times 10^{28} \mu \bar{\mu} - \frac{(\epsilon_0 - 1)(2\epsilon_0 + 1)}{9\epsilon_0} v + R \right] \quad (3)$$

where $\mu \bar{\mu}$ is the scalar product of the dipole moment, μ of the solute and dipole moment, $\bar{\mu}$ of the solute and its shell of neighbours, beyond which the dielectric constant equals the macroscopically observed dielectric constant. ϵ_0 is the dielectric constant of the solvent, v is the molar volume of the solute and R is its molar refractivity. Therefore, a decrease in dielectric increment also decreases Keesom interaction. In general, the decrease in methanol composition increases dielectric constant of mobile phase and thus decreases dielectric increment by eqn.(3). The solvent shell of increased dielectric constant causes an increase in electrostatic shielding effect and thus results in a decrease in the effective dipole moment of solute. As a result, Keesom interaction is reduced and thus solute retention is increased.

Figure 2 and 3 are the plots of alkylbenzenes and halobenzenes, respectively. Since these solutes do not form hydrogen bondings, only the dielectric constant contributes to the solute retention and thus the natural logarithm of retention factor ($\text{Ln } k'$) is linearly dependent on ϵ' . In the case of halobenzenes, the points are closely located around the line. This is due to their similar dipole moments.

Figure 4, 5 and 6 show the interactions between the solute and mobile phase, water-methanol mixture, on the μ -Bondapak phenyl column. Different trend from Figure 1 was observed in Figure 4. This may be the result of interaction between the solute and phenyl group of the stationary phase which has been ignored in case of the C_{18} column. However, Figure 5 and 6 show similar tendency to Figure 2 and 3 since alkylbenzenes and halobenzenes do not form hydrogen bondings. Thus, the observed retention behavior can be seen

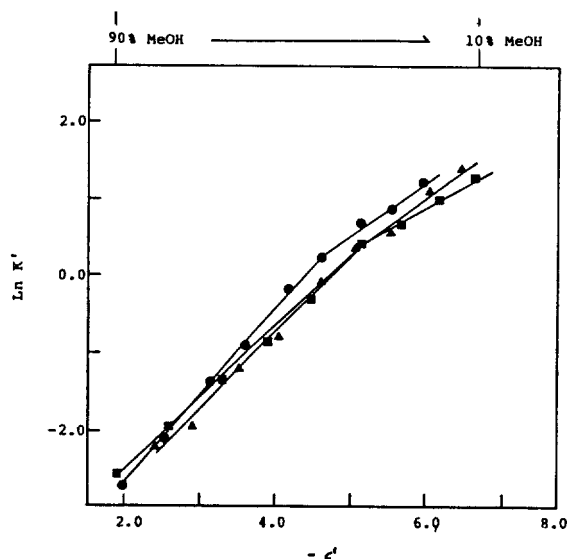


Figure 4. Relationship between dielectric increment ($-\epsilon'$) and $\text{Ln } k'$ values of phenol(●), aniline(▲), and benzyl alcohol(■) on the μ -Bondapak phenyl column.

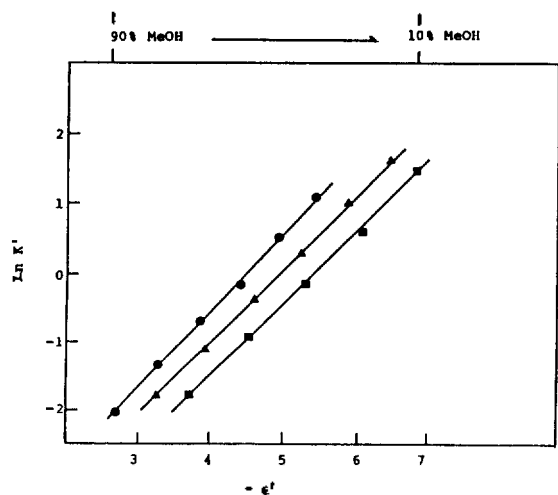


Figure 5. Relationship between dielectric increment ($-\epsilon'$) and $\text{Ln } k'$ values of benzene(●), toluene(▲), and ethyl benzene(■) on the μ -Bondapak phenyl column.

that phenyl column shows different behavior for the high-polarity solutes such as phenol, aniline, and benzyl alcohol whereas it shows similar behavior for the low-polarity solutes compared with C_{18} column.

As examined above, the use of dielectric increment, which represent the interaction between the solute and the solvent adjacent to the solute, will be helpful to get a quantitative relationship on the solute retention.

Effect of Solubility Parameter on Solute Retention.

The correlation between the solute retention and solubility parameter has been examined because the solute-mobile phase interaction is related to solubility. In condensed phases (solids, liquids, solutions) strong attractive forces exist between molecules, and as a result each molecule has a considerable (negative) potential energy. This potential energy is called the cohesive energy, $-E$. The correlation between the cohesive energy per unit volume (cohesive energy density) and solubility parameter δ is⁹

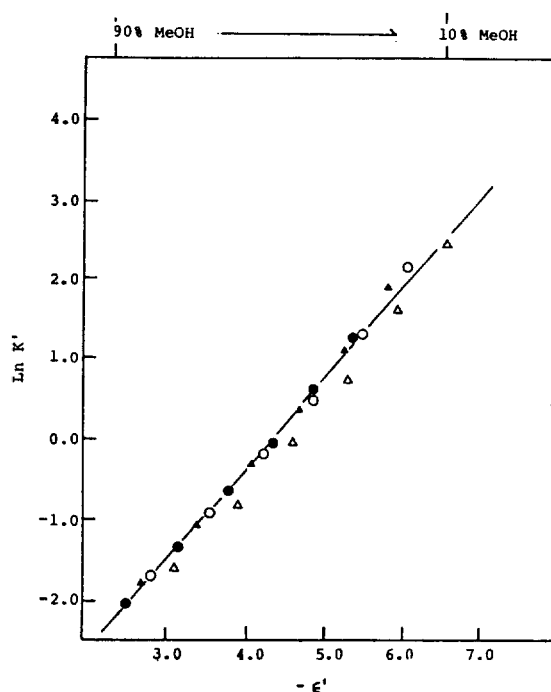


Figure 6. Relationship between dielectric increment ($-\epsilon'$) and $\text{Ln } k'$ values of fluorobenzene(●), chlorobenzene(▲), bromobenzene(○), and iodobenzene(△) on the μ -Bondapak phenyl column.

Table 3. Physical Properties of Mono-substituted Benzenes^a

| Sample | MW | MV | ϵ | μ |
|----------------|--------|--------|------------|-------|
| Benzene | 78.11 | 88.86 | 2.28 | 0.00 |
| Toluene | 92.13 | 106.40 | 2.38 | 0.36 |
| Ethylbenzene | 106.16 | 122.46 | 2.40 | 0.59 |
| Fluorobenzene | 96.10 | 93.86 | 5.42 | 1.60 |
| Chlorobenzene | 112.56 | 101.77 | 5.62 | 1.69 |
| Bromobenzene | 157.02 | 105.03 | 5.40 | 1.70 |
| Iodobenzene | 204.02 | 111.85 | 4.63 | 1.70 |
| Phenol | 94.11 | 87.87 | 9.78 | 1.45 |
| Aniline | 93.13 | 91.13 | 6.89 | 1.53 |
| Benzyl alcohol | 108.13 | 103.60 | 13.60 | 1.71 |

MW: Molecular weight MV: Molar volume (cm^3/mole) ϵ : Dielectric constant ($\text{C}^2/\text{J}\cdot\text{m}$) μ : Dipole moment (D) ^aReference 9.

$$\delta = \left(-\frac{E}{V}\right)^{1/2} \tag{4}$$

There are three modes of interaction between molecules which collectively produce the cohesive energy characteristic of the liquid state: (i) dispersion or London force; (ii) polar interactions; (iii) specific chemical interactions, notably hydrogen bonding.

$$-E = -E_d - E_p - E_h \tag{5}$$

$$-\frac{E}{V} = -\frac{E_d}{V} - \frac{E_p}{V} - \frac{E_h}{V}$$

or $\delta_o^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$ (6)

The solubility parameter values of solutes and solvents used in this study are shown in Table 3. In general, δ_o values de-

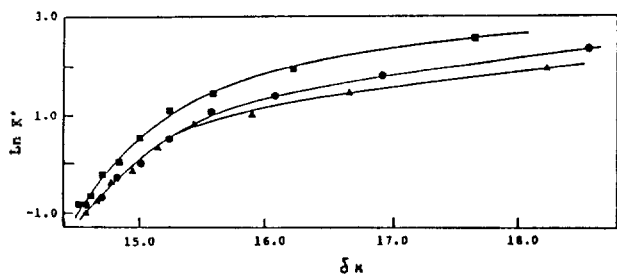


Figure 7. Plots of $\ln k'$ vs. δ_M of phenol(●), aniline(▲), and benzyl alcohol(■). The chromatographic conditions are the same as in Figure 1.

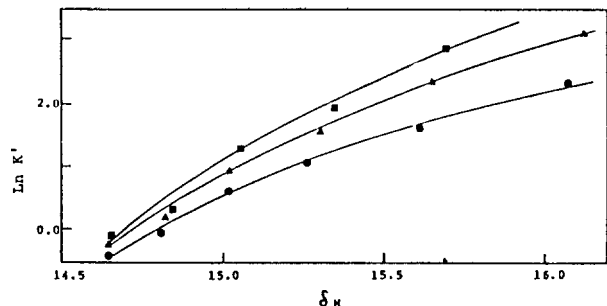


Figure 8. Plots of $\ln k'$ vs. δ_M of benzene(●), toluene(▲), and ethylbenzene(■). The chromatographic conditions are the same as in Figure 1.

crease regularly with increasing E_d , indicating the dominating contribution to δ_o of polar and hydrogen bonding forces in most liquids.

The solubility parameter of a solute in the binary solvent mixture, δ_M is defined by using an "effective volume fraction", Φ^* term.¹⁰ This term reflects the nearest neighbour solvent environment of a solute with the preferential solvation by one of the solvent components.

$$\delta_M = \Phi_1^* \delta_1 + \Phi_3^* \delta_3$$

$$\frac{\Phi_1^*}{\Phi_3^*} = \frac{\Phi_1 (\delta_2 - \delta_3)^2}{\Phi_3 (\delta_2 - \delta_1)^2}, \quad \Phi_1^* + \Phi_3^* = 1 \quad (7)$$

where δ is the solubility parameter, Φ is volume fraction, subscripts M , 1, 2, and 3 denote mixed solvent, water, solute, and methanol, respectively. Volume fraction, Φ is defined as¹¹

$$\Phi_1 = \frac{n_1}{n_1 + mn_3}, \quad \Phi_3 = \frac{mn_3}{n_1 + mn_3} \quad (8)$$

where n is the mole of solvent and m is the molar volume ratio of water and methanol.

Figure 7, 8 and 9 are the plots of solute retention as a function of solubility parameter of mixed solvent, δ_M in water-methanol mixtures by varying composition on the μ -Bondapak C_{18} column. As the composition of mobile phase changes progressively from pure water to pure methanol, cohesive energy changes. The change in cohesive energy affects the energy state between the solute and mobile phase. This results in a change in solubility of solute in mixed mobile phase as expressed by eq. 7.

Krishnan *et al.*¹² showed the following approximate equation for the desolvation enthalpy of solute Y in solvent S

$$(Y)_{g-s} = (Y)_{g-s}^{st} + (Y)_{g-s}^{sp} \quad (9)$$

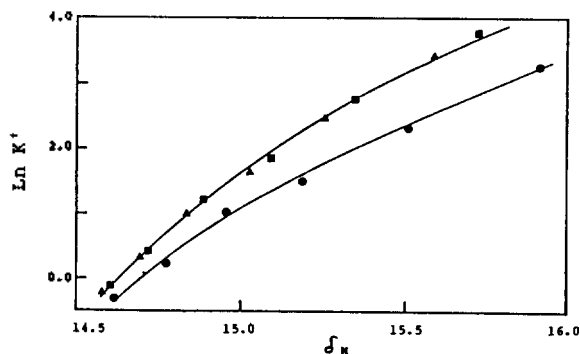


Figure 9. Plots of $\ln k'$ vs. δ_M of chlorobenzene(●), bromobenzene(▲), and iodobenzene(■). The chromatographic conditions are the same as in Figure 1.

Here the electrical contribution derives from the interaction of the electrical dipole of a solvent molecule with the polarizability of the solute. The solubility parameter contribution to eq. (9) is

$$(Y)_{g-s}^{sp} \equiv V_Y \delta_s (2\delta_Y - \delta_s) \quad (10)$$

where V_Y is the molar volume of the solute and the δ_s 's are the solubility parameters of species X . The solubility parameter contribution is again regarded as two terms. The term $-V_Y \delta_s^2$ accounts for the enthalpy associated with the formation of a cavity in the solvent to accommodate the solute particle. The term $2\delta_Y \delta_s$ accounts for the enthalpy of interaction by van der Waals forces of the solute with the solvent molecules next to it in solution.

The linearity of solvation energy cannot be expected as to methanol composition changes in water-methanol mixture. Since the change in solubility parameter with change in cohesive energy is related to the solvation energy of solute, non-linearity between the solute retention and solubility parameter in mixed solvent, δ_M is observed such as the relationship between solute retention and surface tension of mobile phase.² As examined above, the parameters representing the bulk properties of solute, such as solubility parameter, dielectric constant, and polarity are not appropriate to represent the solubility of solute in the system containing the polar non-electrolyte in the reactive solvent. But parameters representing the interaction between solute and the solvent adjacent to the solute are capable of explaining the solute solubility. By using the parameters, dielectric increment ϵ' and mixed solvent solubility parameter δ_M which represent the change occurring between the solute and its adjacent solvent, it is expected to get better results in predicting the retention.

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Comparative Vibrational Spectroscopic Studies Between Nickel, Zinc Tetraphenylporphyrins and Tetraphenylchlorins

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The infrared and resonance Raman spectra are reported for nickel and zinc tetraphenylchlorins. It is found that the IR and RR spectra become more complicated compared with the corresponding porphyrin analogs due to the symmetry changes. Some vibrational parameters like the core size and the symmetry change are examined in accordance with vibrational spectra of other type of chlorins.

Introduction

The vibrational spectroscopic studies on the metalloporphyrin through infrared (IR) and Raman spectroscopies have been actively carried out for the last 10 years.¹ The metalloporphyrins are model compounds which have been extensively studied *in vitro* to understand the nature of chemical bonds or the geometrical structure of macrocycle molecules and the electron transfer reaction or O₂ transfer mechanism in photosynthesis.² In metalloporphyrins the transition metal is inserted into the center of the extended aromatic ring; due to the long conjugation bond, there is a very strong absorption band in the visible range (Figure 1).³ The *d* orbital of the central metal has a strong effect on the vibrational structure of the metalloporphyrin; consequently the spin state, the oxidation state and the size of the metal or the axial ligand effect have been examined relatively well through vibrational spectroscopic studies.

In metallochlorins the C_β-C_γ bond of one of four pyrrole rings of the metalloporphyrin is saturated by hydrogens (Figure 1). Metallochlorins contribute to the biological catalytic function not only in chlorophylls but also in the prosthetic groups of various heme proteins, like metalloporphyrins.⁴⁻⁸ Some resonance Raman (RR) and IR spectroscopic studies on chlorophylls,⁹ bacterial cytochrome *d*,¹⁰⁻¹² leukocyte meylperoxidase,^{7,8} bovine spleen green heme protein⁸ and sulfmyoglobin⁵ have been reported. For the model compound, reports on RR spectra of M(II)OEC,¹³⁻¹⁶ Ni(II)TMC¹⁷ and Cu(II)TPC¹⁷ were published by several groups and quite

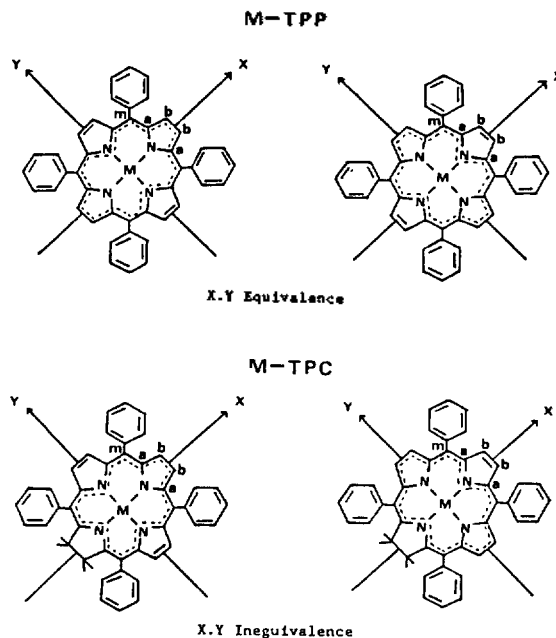


Figure 1. Inner π electron conjugation pathways for a metalloporphyrin and a metallochlorin. a, b, m denote different carbon positions respectively and M represents a metal.

recently the problem of assigning the chlorin vibrational spectrum was addressed by Bocian *et al.*¹⁸ However, if the criteria of distinguishing between the porphyrin and the chlorin RR spectroscopic parameters are to be widely applicable to the verification of the presence of the chlorin

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