Properties of the Solute–Stationary Liquid Interactions in Gas Liquid Chromatography

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Received November 12, 2007; accepted December 14, 2007; published online December 18, 2007

The solute–stationary liquid interaction in gas liquid chromatography (GLC) was determined using Eyring's model. The interaction was determined to be the physical adsorption. The descriptor σ_M was derived and estimated by van der Waals interactions. The CH/ π interaction energies were calculated by Tsuzuki *et al.* using the high-level *ab initio* calculations. The CH/ π interaction energy was concluded to consist of the dispersion energy (E_{dis}) rather than the electrostatic (E_{es}) and charge-transfer (E_{ct}) energies. These energies were in good agreement with our descriptor σ_M . Furthermore, the macroscopic σ_M also had microscopic support through the weak CH/ π interactions. In substituted benzenes, regression analyses were carried out using σ_M for the relative retention values, $\log \gamma$, as a measure of the solute–stationary liquid interaction. The analyses revealed good results under non-polar conditions. The $\log \gamma$ values therefore consisted primarily of contributions from the dispersion interaction and the CH/ π complex. Moreover, these values were useful when added to the electrostatic term (our descriptor σ_{es}) for polar solutes. That is, the $\log \gamma$ values were estimated by the regression analyses using both σ_M and σ_{es} , and were in good agreement with the predicted values.

Key words physical adsorption; van der Waals interaction; CH/ π interaction; gas liquid chromatography; solute–stationary liquid interaction; substituted benzene

Noncovalent interactions are very important in molecular recognition of biochemistry, molecular crystals,^{1–3)} and host-guest complexes.⁴⁾ In addition, they play a key role in determining the molecular orientation in molecular assemblies. The weak interaction between the C–H bond and the aromatic π system called the CH/ π interaction,⁵⁾ has been determined to be a primary contributor to the electrostatic and charge-transfer terms^{5,6)} based on primary *ab initio* calculations using a small basis set. In recent years, high-level *ab initio* calculations of the typical CH/ π complex have shown that dispersion is a major source of attraction.^{7–9)} MP2 interaction energy depends strongly on the basis set and small basis sets (6-31G*, 6-311G** and cc-pVDZ) greatly underestimate the attraction. Therefore, MP2/cc-pVXZ (X=T or Q) or MP2/aug-cc-pVXZ (X=D or T) level calculations are necessary for quantitative evaluation of the dispersion energy.¹⁰⁾ The estimated CCSD(T) interaction energy for a methane–benzene complex as an example of a typical CH/ π interaction at the basis set limit (D_e) was reported to be $-1.43 \text{ kcal mol}^{-1}$ by Shibasaki *et al.*¹⁰⁾ Takahashi *et al.*¹¹⁾ reported a value of $-1.01 \text{ kcal mol}^{-1}$ for the same structure using MP2/6-311++G (d,p) level calculations. The binding energy D_0 was estimated by the D_e and vibrational zero-point energy. This value showed that the former D_0 ($1.13 \text{ kcal mol}^{-1}$) was close to the experimental D_0 (1.03 – $1.13 \text{ kcal mol}^{-1}$). Furthermore, DEF calculations were discussed using BLYP, B3LYP, PW91 and PBE functions were determined to be in appropriate for the quantitative evaluation of the CH/ π interaction energy.^{12–14)} The calculated energy $E_{\text{CCSD(T)}(\text{limit})}$ was determined to be appropriate for a quantitative evaluation of the CH/ π interaction.

In the solute–stationary liquid interaction of gas liquid chromatography, the entropy changes $\Delta\Delta S_s^\circ$ of dissolution were determined to be correlated to the descriptor σ_M in order to evaluate a physical adsorption using Eyring's model.^{15,16)} These findings supported the fact that van der Waals interactions were responsible for the formation CH/ π

complexes between C–H bond of squalane as the stationary liquid and the aromatic π system of the solute. Herein, we discuss the physical origin of the microscopic conditions under which the descriptor σ_M is correlated to the CH/ π interaction energy introduced into the high-level *ab initio* calculations.

Experimental

Relative Retention Value $\log \gamma$ The $\log \gamma$ defined by Eq. 1.¹⁷⁾

$$\log \gamma = \log[t_R(B)/t_R(A)] = -[\Delta H_s^\circ(B) - \Delta H_s^\circ(A)]/2.303RT + [\Delta S_s^\circ(B) - \Delta S_s^\circ(A)]/2.303R \quad (1)$$

Where $t_R(A)$ and $t_R(B)$ are the retention times of the reference and substituted benzenes, respectively. ΔH_s° and ΔS_s° denote the enthalpy and entropy of dissolution of A and B. All data for $\log \gamma$ and the thermodynamic parameters were cited in references,^{18–20)} and the regression analyses were carried out using the statistical program.²¹⁾

Descriptors σ_M and σ_{es} for Regression Analysis The descriptor σ_M was derived from the Eyring's method: The activated translational entropy change $\Delta\Delta S_{\text{ABC}}^\dagger$ for Eyring's equation¹⁵⁾ is given by the following equation, when there is the interaction between the solutes (A and B are the reference and its derivatives) and the non-polar stationary liquid (where C is constant).

$$\Delta S_{\text{AC}}^\dagger = -R \ln[(2\pi m_A kTe)^{3/2}/h^3] \quad (2)$$

$$\Delta S_{\text{BC}}^\dagger = -R \ln[(2\pi m_B kTe)^{3/2}/h^3] \quad (3)$$

Where R , k , T and h are the gas constant, Boltzmann's constant, absolute temperature and Plank's constant, respectively.

$$\Delta\Delta S_{\text{ABC}}^\dagger = \Delta S_{\text{BC}}^\dagger - \Delta S_{\text{AC}}^\dagger = -3/2R \ln[2\pi m_B kTe/2\pi m_A kTe] \quad (4)$$

When T is constant, Eq. 5 is given by,

$$\Delta\Delta S_{\text{ABC}}^\dagger = -3/2R \ln(m_B/m_A) \quad (5)$$

where m_A and m_B take the relative molecular mass (M_A and M_B) and $\Delta\Delta S_{\text{ABC}}^\dagger$ becomes the linear relation $\ln(M_B/M_A)$. The $\ln(M_B/M_A)$ can now be replaced with the descriptor σ_M as follows,

$$\ln(M_B/M_A) = 2.303 \log(M_B/M_A) = \sigma_M \quad (6)$$

$$\Delta\Delta S_{\text{ABC}}^\dagger \propto \sigma_M \quad (7)$$

The descriptor σ_M is evaluates the van der Waals interaction energy as phys-

ical adsorption.

The descriptor σ_{es} can be derived from induction and orientation energies: Induction energy is defined by the following equations:

$$E_{\text{ind, AC}} = -[(\alpha_A \mu_C^2 + \alpha_C \mu_A^2)]/r_{\text{AC}}^6 \quad (8)$$

$$E_{\text{ind, BC}} = -[(\alpha_B \mu_C^2 + \alpha_C \mu_B^2)]/r_{\text{BC}}^6 \quad (9)$$

α and μ are polarizability²²⁾ and dipole moment,²³⁾ respectively. When r_{AC}^6 and r_{BC}^6 equal $\alpha_A \alpha_C$ and $\alpha_B \alpha_C$, and μ_C^2/α_C is the constant, both $E_{\text{ind, AC}}$ and $E_{\text{ind, BC}}$ are correlated to μ_A^2/α_A and μ_B^2/α_B , respectively.

The descriptor σ_{es} is defined by the following equation,

$$\sigma_{\text{es}} = \log[(\mu_B^2/\alpha_B)/(\mu_A^2/\alpha_A)] \quad (10)$$

The μ_A of benzene reference is 0.31 $D^{24,25)}$ for $\mu_{\text{Csp}^3\text{-H}}$.

$\Delta E_{\text{ind, ABC}}$ is related to σ_{es} and the orientation energy change $\Delta E_{\text{ori, ABC}}$ is defined by,

$$\Delta E_{\text{ind, ABC}} \propto \sigma_{\text{es}} \quad (11)$$

$$\Delta E_{\text{ori, ABC}} \propto \sigma_{\text{es}} \quad (12)$$

The descriptor σ_{es} can be evaluated by both induction and orientation energies, and is identical to the electrostatic interaction energy.

Results and Discussion

Relation between Interaction Energy of Substituted Methane-Benzene and Methane-Substituted Benzene Complexes and the Descriptor σ_{M} The electrostatic and charge-transfer terms have been reported to be very important based on the primary calculations of CH/ π complexes.^{5,6)} However, typical CH/ π complexes such as benzene-methane⁷⁻⁹⁾ have been shown primarily of dispersion interactions based on high-level *ab initio* calculations. The interaction energies were also consistent with the experimental binding energy D_0 of benzene-X (X =methane,¹⁰⁾ ethylene and acetylene,²⁶⁾ and benzene^{27,28)} as CH/ π complexes and benzene-XH₂ (X =N²⁹⁾ and O³⁰⁻³²⁾ as the T-shape form of hydrogen bonds. Both the calculated and experimental binding energies in the weak interaction showed a linear correlation, as shown in Fig. 1.

Therefore, the high-level *ab initio* calculation is suitable for the evaluation of the CH/ π interaction energy as the dispersion interaction is the major source of the attraction. Results of the calculation suggested that σ_{M} values were good linear relations to the total energy E_{total} of the typical complexes such as methane-benzene³³⁾ and activated complexes such as halomethane-benzene^{8,34)} as shown in Fig. 2. The interaction between the acidic CH group and π -electrons in the halomethane-benzene complex was categorized as a conventional π -hydrogen bond rather than as a van der Waals interaction.³⁵⁾ The large slope observed in Fig. 2 represents the halomethane-benzene series, and the difference between the two slopes accounts for the electrostatic interaction.

The regression analyses of E_{total} are given by,

$$-E_{\text{total}} = 5.16(0.51)\sigma_{\text{M}} - 2.51(0.47) \quad (13)$$

$$n=14, r=0.946, F=102.0, \text{S.D.}=0.17$$

(CH₄-C₆H₆, -C₆H₅Me, -C₆H₄Me₂, -C₆H₃Me₃, -C₁₀H₈, C₆H₆-C₂H₆, -CH₃NH₂, -CH₃OH, -CH₃OCH₃, -C₆H₆, -C₆H₅CH₃, -C₆H₅OH, -C₆H₅F, -C₆H₅CN)

$$-E_{\text{total}} = 12.20(0.94)\sigma_{\text{M}} - 7.81(0.86) \quad (14)$$

$$n=12, r=0.972, F=169.2, \text{S.D.}=0.29$$

(C₆H₆-CH₄, C₆H₆-C₂H₄, -C₂H₂, -CH₃F, -CH₃Cl, -CH₂CINH₂, -CH₂CIOH, -CH₂Cl₂, -CH₂FCl, -CH₂F₂, -CHCl₃, -CHF₃)

Fig. 1. Correlation between the Calculated and Experimental Binding Energies $D_0/\text{kcal mol}^{-1}$ with Benzene Complexes

Fig. 2. Plots of CH/ π Interaction Energy E_{total} versus the Descriptor σ_{M}
○, ● and ◎ estimated E_{total} by Tsuzuki *et al.* and Morita *et al.*, and by Sinnokrot *et al.*,³⁸⁾ respectively.

$$-E_{\text{total}} = 6.82(0.53)\sigma_{\text{M}} - 0.82(0.06)E_{\text{es}} - 4.11(0.49) \quad (15)$$

$$n=25, r=0.976, F=225.5, \text{S.D.}=0.23$$

These findings suggest that the typical and activated CH/ π complexes consisted primarily of the dispersion energy E_{dis} (Eqs. 13, 14). The difference of two groups is E_{es} and it is negligible small for the typical CH/ π complex. The two groups (Eqs. 13, 14) could be defined by one equation as in Eq. 15, since E_{es} contributed to the activated CH/ π complex. The typical CH/ π complex differs from the hydrogen bond and the orientation dependence is very small. On the other hand, the activated CH/ π complex is close to weak hydrogen bond as C₆H₆-H₂O *etc.*³⁶⁾ The descriptors σ_{M} will be compared with the correlation interaction energy E_{corr} in the following section.

The Relationship between E_{corr} and σ_{M} The relationship between E_{corr} and σ_{M} was linear up to relative large energy values in the activated CH/ π interaction. The relationship could be described by the following regression analyses, as shown in Fig. 3.

$$E_{\text{corr}} = -17.03(1.92)\sigma_{\text{M}} + 11.45(1.78) \quad (16)$$

$$n=9 \text{ (C}_6\text{H}_6\text{-CH}_3\text{F, -CH}_3\text{Cl, -CH}_2\text{CINH}_2\text{, CH}_2\text{CIOH, -CH}_2\text{Cl}_2\text{, -CH}_2\text{FCl, -CHCl}_3\text{, -C}_2\text{H}_2\text{, -CH}_4\text{)}, r=0.958, F=78.9, \text{S.D.}=0.54$$

The σ_{M} is proposed to be representative of the E_{dis} , since the E_{corr} consists primarily of attractive dispersion energy.

The Relationship between E_{es} and σ_{es} Hartree-Fock

(HF) calculation does not depend on the basis set. Therefore, the descriptor σ_{es} values were comparable with the electrostatic energies E_{es} using MP2/6-31G*(0.25) in pyridine-substituted benzenes complexes³⁷⁾ (Fig. 4).

This regression analyses is given by,

$$\Delta E_{\text{es}} = -0.23(0.04)\sigma_{\text{es}} - 0.08(0.06) \quad (17)$$

$n=8$ (H, Me, OH, NH₂, CHO, COOH, CN, NO₂), $r=0.905$, $F=27.0$, S.D.=0.09

Fig. 3. Correlation between E_{corr} and the Descriptor σ_{M} in Benzene–Methanes and Methane–Benzenes Complexes

● and ○ are chloro- and substituted compounds, respectively.

Fig. 4. Correlation between $-\Delta E_{\text{es}}$ of Pyridine–Monosubstituted Benzenes Complexes and the Descriptor σ_{es}

The two descriptors σ_{M} and σ_{es} were in good agreement with E_{corr} and E_{es} in Eqs. 16 and 17, respectively. Therefore, both descriptors could be used to estimate the relatively weak interaction. Next, regression analyses were carried out using σ_{M} and σ_{es} in the solute–stationary liquid interaction.

The Relation between σ_{M} and $\Delta\Delta S_s^\circ$ The activated translational entropy change $\Delta\Delta S_s^\dagger$ derived using Eyring's model could be correlated with σ_{M} . Furthermore, these thermodynamic parameters were obtained, because the relative retention values, $\log \gamma$, varied with temperature. If the interactions were based on physical adsorption, the resolution entropy changes $\Delta\Delta S_s^\circ$ would be related to σ_{M} . The $\Delta\Delta S_s^\circ$ (np) values showed a linear relationship for mono-substituted benzenes–squalane under non-polar conditions. (Fig. 5).

These results suggested that the solute–stationary liquid interaction primarily consisted of van der Waals interactions, which was reflected in the physical adsorption. Table 1 shows a list of regression analyses for mono-, 1,3- and 1,4-substituted benzenes under non-polar conditions. The predicted values were fitted to the observed values (Fig. 6).

The $\Delta\Delta S_s^\circ$ (sp) values estimated under semi-polar conditions as (dinonyl phthalate) were also analyzed using σ_{M} . Furthermore, the values were well fit in addition to descriptor σ_{es} . When the stationary phase was polar, the contribution from σ_{es} was significant. The solute–stationary liquid inter-

Fig. 5. Correlation between the Entropy Change $\Delta\Delta S_s^\circ$ and the Descriptor σ_{M} in Substituted Benzenes

●=R, H; ◆=F, R; ○=Cl, R; ◇=Br, R; △=I, R compounds.

Table 1. The Results of the Regression Analyses for the Resolution Entropy Changes $\Delta\Delta S_s^\circ$ and Relative Retention Values, $\log \gamma$, in for the Solute–Squalane Interactions for Substituted Benzenes

	Coeff. of σ_{M}	Coeff. of σ_{es}	Const.	$n^a)$	$r^b)$	$F^c)$	S.D. ^{d)}
$-\Delta\Delta S_s^\circ$	206.64 (11.57)		2.41 (1.51)	13	0.982	296.6	2.16
$-\Delta\Delta S_s^\circ$	190.64 (15.18)		−145.95 (13.88)	8	0.982	157.8	2.41
$-\Delta\Delta S_s^\circ$	165.61 (15.05)		−117.18 (14.35)	9	0.972	121.2	1.65
$-\Delta\Delta S_s^\circ$	195.25 (13.74)		−164.56 (14.71)	12	0.976	201.9	1.76
$-\Delta\Delta S_s^\circ$	206.64 (11.57)		−192.28 (13.47)	7	0.992	318.9	1.25
$-\Delta\Delta S_s^\circ$	143.56 (5.93)		−98.54 (5.61)	49	0.962	585.8	3.49
$\log \gamma$	4.308 (0.334)		−2.936 (0.288)	13	0.968	165.9	0.089
$\log \gamma$	3.934 (0.246)	0.087 (0.023)	−2.696 (0.204)		0.987	190.68	0.060
$\log \gamma$	4.247 (0.226)		−2.935 (0.213)	18	0.978	353.7	0.085
$\log \gamma$	3.842 (0.226)	0.087 (0.028)	−2.661 (0.194)		0.987	274.2	0.068
$\log \gamma$	4.626 (0.254)		−3.199 (0.243)	13	0.984	332.9	0.093
$\log \gamma$	4.196 (0.217)	0.108 (0.031)	−2.953 (0.185)		0.993	342.4	0.066
$\log \gamma$	4.942 (0.331)		−3.462 (0.317)	24	0.954	222.5	0.143
$\log \gamma$	3.959 (0.279)	0.179 (0.032)	−2.775 (0.241)		0.982	277.9	0.091
$\log \gamma$	4.653 (0.188)		−3.236 (0.178)	64	0.953	614.8	0.123
$\log \gamma$	4.099 (0.165)	0.126 (0.019)	−2.886 (0.145)		0.973	549.9	0.094

a,b,c,d) The number of data, correlation coefficient, variance ratio and standard deviation, respectively.

Fig. 6. Correlation between the Predicted and Observed Entropy Changes $\Delta\Delta S_s^\circ/\text{J mol}^{-1} \text{K}^{-1}$ in Substituted Benzene–Squalane Complexes

Fig. 7. Correlation between the Predicted and Observed $\log \gamma$ in Substituted Benzene–Squalane Complexes

action however consisted with primarily van der Waals interactions. Further the standard coefficients for σ_M were greater than 98% and 80% under non- and semi-polar conditions, respectively, in GLC.

$$-\Delta\Delta S_s^\circ(\text{np}) = 131.79(7.44)\sigma_M + 1.62(0.69)\sigma_{\text{es}} + 2.01(1.28) \quad (18)$$

$n=13$ (H, Me, Et, *n*-Pr, *n*-Bu, OMe, OEt, COMe, COEt, CO₂Me, CO₂Et, CN, NO₂), $r=0.988$, $F=211.0$, S.D.=1.82

$$-\Delta\Delta S_s^\circ(\text{sp}) = 147.67(9.39)\sigma_M + 6.71(0.88)\sigma_{\text{es}} + 3.35(1.61) \quad (19)$$

$n=13$, $r=0.990$, $F=241.5$, S.D.=2.30

Regression Analyses of the Relative Retention Value $\log \gamma$ The relative retention values $\log \gamma$ were analyzed using two descriptors σ_M and σ_{es} for mono- and di-substituted benzenes–squalane interactions under non-polar conditions (Table 1).

The observed values for $\log \gamma$ were in good agreement with predicted values (Fig. 7). Therefore, the descriptor σ_M is expected to be useful for determining the relative contribution of very weak interactions such as the CH/ π interaction.

Conclusion

The solute–stationary liquid interaction in GLC was determined using Eyring’s model to be the physical adsorption.

The descriptor σ_M derived using Eyring’s model was used to estimate the van der Waals interactions and was in good agreement with the CH/ π interaction energy introduced into high-level *ab initio* calculations. This suggested that the solute–stationary liquid interaction for halo-benzenes consisted primarily of van der Waals interactions under the gas conditions. In other words, the induced macroscopic σ_M was correlated with the microscopic high-level calculated energy as the CH/ π interaction. Regression analyses of the $\log \gamma$ values were carried out using σ_M and the predicted values were determined to be in good agreement with the observed values.

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