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On the Solute-Stationary Phase Interaction in Gas Liquid Chromatography. Relative Retention Values for Mono-substituted Benzene Derivatives and Their Energy Partition by Means of Regression Analysis

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Thermodynamic parameters were determined by variable temperature experiments on the gas-liquid chromatography (GLC) relative retention values, log γ, of mono-substituted benzene derivatives. The free energy change $\Delta\Delta G_s^\circ$ which is estimated from the enthalpy $\Delta\Delta H_s^\circ$ and the entropy $\Delta\Delta S_s^\circ$ at 298 K is less than $-15\,\mathrm{kJ\cdot mol^{-1}}$, corresponding to an interaction between the sample and the liquid stationary phase. With regards to the co-linearlity with the standard entropy $S^\circ(B\cdot\cdot C)$ of the complex, between the sample and the liquid stationary phase, an excellent linear relationship of $\Delta\Delta S_s^\circ$ with the electron-donating and -withdrawing groups was obtained. The log γ can also be expressed by the linear combination of the descriptors σ_{s°, μ^2/α, and σ_R which are the dispersion and repulsion, the induction and orientation, and the charge transfer interaction energies respectively, and from the evaluation of the standard coefficient by the *z*-score of log γ, $(E_{\mathrm{dis}}+E_{\mathrm{rep}})>E_{\mathrm{CT}}>(E_{\mathrm{ind}}+E_{\mathrm{ori}})$. Under non-polar conditions, $(E_{\mathrm{dis}}+E_{\mathrm{rep}})$ was dominant while under polar conditions, the ratio of $[(E_{\mathrm{ind}}+E_{\mathrm{ori}})+E_{\mathrm{CT}}]$ increased to the level of $(E_{\mathrm{dis}}+E_{\mathrm{rep}})$.

Keywords gas liquid chromatography; relative retention value log γ; interaction energy; thermodynamic parameter; substituent entropy constant σ_{s°; monosubstituted benzene derivative

In a previous report,1) which assumed that gas-liquid chromatography (GLC) corresponds to a weak molecular interaction, we analyzed the relative retention values log γ, using three kinds of descriptors which were derived from molecular structure theory.

In this paper, we report that the free energy variations of dissolution, $-\Delta\Delta G_s^\circ$, estimated from the variable temperature experiments involving log γ correspond to the sample–liquid stationary phase interaction and are less than $15\,\mathrm{kJ\cdot mol^{-1}}$ under both non-polar and polar conditions. In general, the hydrogen bonding energy is below $40\,\mathrm{kJ\cdot mol^{-1}}$, and therefore, the GLC interaction is a weak molecular one.

Next, the regression analysis based on this weak molecular interaction was carried out using three types of descriptors, σ_{s°, μ^2/α,2) and σ_R.3) The descriptor σ_{s° comes from evaluation of the force constants determined by the modified Lennard–Jones (12, 6) potential equation and represents the dispersion E_{dis} and repulsion E_{rep} energies. The descriptor μ^2/α was introduced by the classical equations4) of the orientation E_{ori} and induction E_{ind} energies, when $\alpha_A\alpha_B$ values were proportional to r_{AB}^6. The substituent constant of resonance effect σ_R was derived from gas phase proton transfer equilibria by R. W. Taft *et al.* and represents the charge transfer interaction energy E_{CT}. The relative magnitudes of these three descriptors were obtained from the standard coefficient *z*-score and the ratio of $(E_{\mathrm{dis}}+E_{\mathrm{rep}})$ and $[(E_{\mathrm{ind}}+E_{\mathrm{ori}})+E_{\mathrm{CT}}]$ was obtained.

Experimental

Relative Retention Value log γ and Experimental Conditions for GLC The log γ is defined by Eq. 15) below.

$$\log\gamma=\log[t_R(B)/t_R(A)]=-[\Delta H_s^\circ(B)-\Delta H_s^\circ(A)]/2.303\boldsymbol{R}T+[\Delta S_s^\circ(B)-\Delta S_s^\circ(A)]/2.303\boldsymbol{R}=-[\Delta G_s^\circ(B)-\Delta G_s^\circ(A)]/2.303\boldsymbol{R} \qquad (1)$$

Here $t_R(A)$ and $t_R(B)$ are the retention times of the reference and substituted benzenes, respectively. ΔG_s°, ΔH_s° and ΔS_s° denote the free energy, enthalpy and entropy of dissolution of A and B. Measurements were obtained using a Shimazu 8A Type gas liquid chromatograph.

Measurement Conditions Sample mono-substituted benzene derivatives; reference, benzene; mobile phase, nitrogen (N_2); stationary phase, Chromosorb W(AW-DMCS) + 20% squalane or 20% dinonyl phthalate (DNP); column temperature, 388—418 K, temperature measured to ±0.1 K using a CA thermocouple.

Regression Analysis Regression analyses were carried out according to Eq. 2, using the program MVA.6)

$$\log\gamma=a\sigma_{s^\circ}+b\sigma_R+c\mu^2/\alpha+d \qquad (2)$$

Here σ_{s° and μ^2/α represent (E_{dis} and E_{rep}), (E_{ind} and E_{ori}) respectively, and the additional descriptor σ_R3) was employed as a descriptor for the charge–transfer interaction energy E_{CT}.

Normalization of the Regression Coefficient *Z*-Scores of the regression analyses are also given using the program MVA.6) The standard coefficients of the three descriptors are nomalized by Eq. 3:

$$a'^2+b'^2+c'^2=1 \qquad (3)$$

Descriptors for Regression Analyses Substituent Entropy Constant σ_{s°: The descriptor is derived from the absolute entropy $S_{298}^\circ(\mathrm{g})$7) by Eq. 4 below;

$$\sigma_{s^\circ}=\log[S_{298}^\circ(\mathrm{g})(B)/S_{298}^\circ(\mathrm{g})(A)] \qquad (4)$$

where A and B represent the reference and its derivatives, respectively. All the descriptors of mono-substituted benzene derivatives were taken from our previous report.8)

Estimation of Absolute Entropy S_{298}°(g) 1. Squalane: The value of σ_{s° for squalane was estimated using Eq. 59):

$$\sigma_{s^\circ}(R_ACH_2R_B)=0.6545\Sigma\sigma_{s^\circ}(A, B)+0.0777 \qquad (5)$$

where some types of components A and B are more favorable than others (*e.g.* when A and B equal methyl and *n*-butyl) and determined as sums of the four following components: A_1, 2,6-dimethylheptane $\sigma_{s^\circ}=0.408$; A_2, 4-methylheptane $\sigma_{s^\circ}=0.386$; B_1, 3-methylhexane $\sigma_{s^\circ}=0.357$; B_2, 2,6-dimethylheptane $\sigma_{s^\circ}=0.408$.

$$\sigma_{s^\circ}=\Sigma\sigma_{s^\circ}(A_1, A_2)+\Sigma\sigma_{s^\circ}(B_1, B_2)=\Sigma\sigma_{s^\circ}(A_{12}, B_{12}) \qquad (6)$$

Thus, σ_{s° of squalane can be determined as 0.841 from Eqs. 5 and 6. The value of $S_{298}^\circ(\mathrm{g})$ $1291.7\,\mathrm{J\cdot mol^{-1}K^{-1}}$ is estimated from Eq. 4 and $186.30\,\mathrm{J\cdot mol^{-1}K^{-1}}$ as $S_{298}^\circ(\mathrm{g})$ for the methane reference.

2. Dinonyl Phthalate (DNP): The estimation of σ_{s° for DNP can be obtained from Eq. 710) using σ_{s°(mono) of 0.435 for *n*-nonyl benzoate;

$$\sigma_{s^\circ}(1, 2)=0.859\Sigma\sigma_{s^\circ}(\mathrm{mono})-0.011 \qquad (7)$$

Thus, σ_{s° of 0.737 is obtained, and $S_{298}^\circ(\mathrm{g})$ of DNP is $1472.6\,\mathrm{J\cdot mol^{-1}K^{-1}}$.

3. Sample–Liquid Stationary Phase Complex: From equilibria expressed by Eqs. 8 and 9;

TABLE I. Values of Entropy Change for Benzene–Squalane (1) and Benzene–DNP (2) ΔS_s° and Standard Entropy for Benzene (A), Stationary Liquid (C) and Benzene–Stationary Liquid Complex (A··C) at 298 K

	$-\Delta S_s^\circ$	S° (A) [J·mol^{-1}K^{-1}]	S° (C)	S° (A··C)
(1)	44.00	269.2	1291.7	1516.9
(2)	48.58	269.2	1472.6	1693.2

TABLE II. The Values of Standard Entropy for Mono-substituted Benzene Derivatives–Liquid Stationary Phase Complex

R	S° (B··C) [J·mol^{-1}K^{-1}]	
	Squalane	DNP
Me	1556.7	1732.7
Et	1588.1	1764.7
OMe	1585.4	1756.3
COMe	1589.8	1757.7
CN	1545.6	1711.1
NO_2	1568.6	1735.4

$$A+C\rightleftharpoons A\cdot\cdot C \tag{8}$$

$$B+C\rightleftharpoons B\cdot\cdot C \tag{9}$$

the entropy change of the equilibrium ΔS_s° is related to the standard entropy by Eqs. 10 and 11;

$$S_s^\circ(A\cdot\cdot C)=S^\circ(A\cdot\cdot C)-[S^\circ(A)+S^\circ(C)] \tag{10}$$

$$S_s^\circ(B\cdot\cdot C)=S^\circ(B\cdot\cdot C)-[S^\circ(B)+S^\circ(C)] \tag{11}$$

From these two equations, the following equation can be derived:

$$\Delta\Delta S_s^\circ=[S^\circ(B\cdot\cdot C)-S^\circ(A\cdot\cdot C)]-[S^\circ(B)-S^\circ(A)]$$

This equation can be rearranged to give Eq. 12.

$$[S^\circ(B\cdot\cdot C)-S^\circ(A\cdot\cdot C)]=\Delta\Delta S_s^\circ+[S^\circ(B)-S^\circ(A)] \tag{12}$$

Thus, S°(B··C) can be obtained if S°(A··C) is known.

a. Estimations of S°(A··C): The value of ΔS_s° for benzene was estimated from the intercept of the linear plot of $\log t_R$(A) *vs.* $1/T$, and S°(A··C) can be estimated from Eq. 10 for benzene–squalane or benzene–DNP complexes as shown in the Table I.

b. Estimation of S°(B··C): The values of S°(B··C) of the mono-substituted benzene derivatives and squalane or DNP complexes were estimated from Eq. 12, using Table II and S°(A··C).

Descriptor μ^2/α Dipole Moment μ: All data are literature values.[11]

Polarizability α: Polarizability values α [$\times 10^{-24}$ cm^3] are given by the Clausius–Mosotti equation, using the refractive indices[12] observed using the sodium D line at 293 K.

Substituent Constant σ_R Data are literature values.[3] In the previous report,[13] because of the nature of GLC conditions, the descriptor σ_R in the gas-phase was employed instead of the substituent (solution) constant σ_π.[14]

Results and Discussion

Temperature-Dependence of log γ Data on the temperature-dependence of log γ, summarized in Table III, give a line with a positive slope when plotted against $1/T\times 10^3$ in Fig. 1, and it shows that $\Delta\Delta H_s^\circ$ should be negative.

The values of $\Delta\Delta H_s^\circ$, $\Delta\Delta S_s^\circ$, and $\Delta\Delta G_s^\circ$[15] at 298 K are summarized in Table IV.

The $\Delta\Delta H_s^\circ$ is compensatory for $\Delta\Delta S_s^\circ$, and $\Delta\Delta G_s^\circ$ also shows a positive slope when plotted against $\Delta\Delta S_s^\circ$ (Fig. 2).

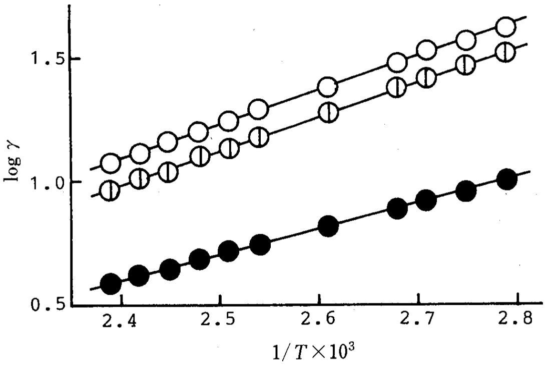

Fig. 1. Correlation between log γ and $1/T\times 10^3$ for Mono-substituted Benzene Derivatives under Polar Conditions

○, NO_2; ⦶, COMe; ●, *tert*-Bu.

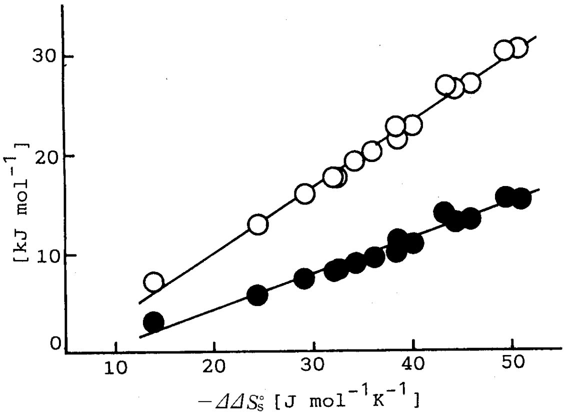

Fig. 2. Correlations between $-\Delta\Delta H_s^\circ$ [kJ·mol^{-1}] (○) or $-\Delta\Delta G_s^\circ$ [kJ·mol^{-1}] (●), and $-\Delta\Delta S_s^\circ$ [J·mol^{-1}·K^{-1}] under Polar Conditions

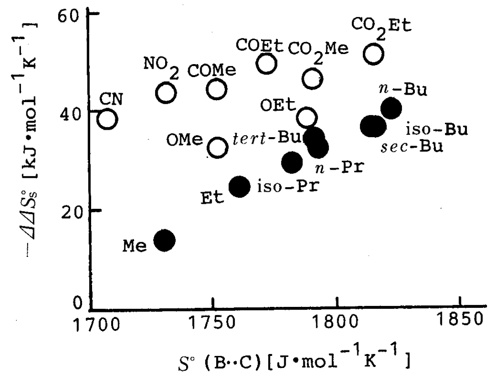

Fig. 3. Correlations between $-\Delta\Delta S_s^\circ$ and S° (B··C) under Non-polar Conditions

●, alkylgroup; ○, others.

All the $-\Delta\Delta G_s^\circ$ values are smaller than 15 kJ·mol^{-1} under both non-polar and polar conditions. The values of $\Delta\Delta S_s^\circ$ correspond to the standard entropy of the complex B··C [S°(B··C) estimated by Eq. 12, Fig. 3], where good linear relations for alkyl groups, excluded OMe, OEt groups, in electron-donating and electron-withdrawing group under non-polar conditions, are given by the Eqs. 13 and 14.

$$-\Delta\Delta S_s^\circ=0.22(0.06)S^\circ(B\cdot\cdot C)-357.62(97.40) \tag{13}$$

$n=8$, $r=0.969$, $F=93.0$, S.D.$=1.95$

$$-\Delta\Delta S_s^\circ=0.14(0.07)S^\circ(B\cdot\cdot C)-210.27(127.58) \tag{14}$$

$n=6$, $r=0.935$, $F=27.9$, S.D.$=2.31$

n, *r*, *F* and S.D. denote the number of data, correlation coefficient, variance ratio and standard deviation, respec-

Table III. Mono-substituted Benzene Derivatives and Their Observed $\log \gamma$ Values at Several Temperatures under Non-polar (1) or Polar (2) Conditions

(1)

		$\log \gamma$ $[1/T \times 10^3]$ (K^{-1})						
		2.39	2.42	2.45	2.48	2.51	2.54	2.57
1	H	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2	Me	0.212	0.219	0.230	0.239	0.251	0.262	0.272
3	Et	0.414	0.429	0.447	0.462	0.484	0.503	0.521
4	*n*-Pr	0.624	0.644	0.670	0.692	0.722	0.749	0.775
5	iso-Pr	0.552	0.571	0.593	0.613	0.642	0.666	0.689
6	*n*-Bu	0.868	0.896	0.931	0.960	0.998	1.033	1.067
7	iso-Bu	0.762	0.784	0.812	0.837	0.873	0.903	0.931
8	*sec*-Bu	0.757	0.782	0.812	0.837	0.871	0.902	0.932
9	*tert*-Bu	0.716	0.740	0.769	0.793	0.826	0.856	0.885
10	COMe	0.770	0.798	0.829	0.856	0.890	0.921	0.952
11	COEt	1.015	1.048	1.087	1.121	1.163	1.203	1.241
12	CO_2Me	0.846	0.873	0.906	0.937	0.974	1.007	1.038
13	CO_2Et	1.029	1.062	1.102	1.138	1.182	1.221	1.259
14	CN	0.528	0.550	0.570	0.588	0.612	0.635	0.663
15	NO_2	0.806	0.831	0.861	0.888	0.922	0.951	0.983
16	OMe	0.478	0.495	0.517	0.536	0.561	0.582	0.602
17	OEt	0.643	0.668	0.697	0.721	0.753	0.782	0.810

(2)

		$\log \gamma$ $[1/T \times 10^3]$ (K^{-1})										
		2.39	2.42	2.45	2.48	2.51	2.54	2.61	2.68	2.71	2.75	2.79
1	H	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2	Me	0.158	0.173	0.184	0.194	0.207	0.220	0.242	0.269	0.283	0.296	0.307
3	Et	0.323	0.349	0.368	0.387	0.411	0.436	0.474	0.522	0.547	0.568	0.591
4	*n*-Pr	0.501	0.535	0.562	0.588	0.621	0.658	0.709	0.774	0.808	0.837	0.866
5	iso-Pr	0.448	0.471	0.491	0.523	0.548	0.570	0.628	0.686	0.715	0.743	0.774
6	*n*-Bu	0.723	0.765	0.801	0.835	0.879	0.927	0.992	1.076	1.120	1.157	1.194
7	iso-Bu	0.612	0.642	0.680	0.711	0.734	0.778	0.844	0.922	0.955	0.991	1.028
8	*sec*-Bu	0.617	0.655	0.685	0.716	0.755	0.797	0.855	0.930	0.969	1.002	1.034
9	*tert*-Bu	0.591	0.619	0.643	0.683	0.713	0.739	0.810	0.881	0.915	0.950	0.985
10	COMe	0.964	1.005	1.038	1.094	1.136	1.172	1.271	1.366	1.415	1.460	1.510
11	COEt	1.173	1.214	1.270	1.316	1.368	1.419	1.520	1.635	1.694	1.731	1.798
12	CO_2Me	0.945	0.994	1.036	1.077	1.131	1.189	1.265	1.363	1.415	1.460	1.503
13	CO_2Et	1.105	1.159	1.207	1.253	1.314	1.379	1.466	1.574	1.634	1.684	1.732
14	CN	0.814	0.845	0.887	0.922	0.960	0.999	1.074	1.160	1.205	1.231	1.283
15	NO_2	1.065	1.104	1.155	1.196	1.240	1.286	1.373	1.477	1.529	1.560	1.623
16	OMe	0.511	0.535	0.567	0.594	0.622	0.652	0.711	0.779	0.815	0.836	0.879
17	OEt	0.645	0.675	0.713	0.746	0.780	0.816	0.887	0.970	1.013	1.039	1.088

tively. S.D. is given by $\text{S.D.} = [S_{se}/(n-k-1)]^{1/2}$, where n and k denote the numbers of observations and variables, and S_{se} denotes the sum of the squares of the residuals. The values within parentheses of the regression equations denote the 95% confidence intervals.

Similarly, $\Delta\Delta H_s^\circ$ and $\Delta\Delta G_s^\circ$ show a linear relationship for values $S^\circ(\mathrm{B}\cdot\cdot\mathrm{C})$ (Fig. 2).

The thermodynamic parameters thus obtained suggest that the equlibria should be considered as weak molecular interactions.

Next, we will discuss $\Delta\Delta G_s^\circ$ from the substituent constants as follows:

Explanation of $\Delta\Delta G_s^\circ$ 1. In our previous report,[16] on the "three-body problem" of GLC, namely, a substrate, mobile gas and liquid stationary phase denoted by 1, 2 and 3, the total free energy change, ΔG_{123}, of a system is given by Eq. 15:

$$\Delta G_{123} = \Delta G_{12} + \Delta G_{23} + \Delta G_{31} + \Delta\Delta G_{123} \tag{15}$$

where ΔG_{12}, ΔG_{23} and ΔG_{31} are the free energy changes of the pairs 1 and 2, 2 and 3 and 3 and 1, respectively; $\Delta\Delta G_{123}$ is the additional minor increment for the whole system. ΔG_{23} is constant when 2 and 3 are specified, and ΔG_{12} is a result of a non-ideal gas mixture of 1 and 2.

2. In GLC, ΔG_{12} is dependent on a large volume of mobile gas, such as nitrogen. ΔG_{12} could therefore be produced by 2 (N_2) and variable samples, and assumed to be negligible. Consequently, at a constant temperature (*e.g.* 298 K), ΔG_{123} is proportional to ΔG_{31}.

Recently, R. W. Taft *et al.*[3] proposed equation 16 from gas phase proton transfer equilibrium, where the substituent constants σ_F, σ_α and σ_R describe the field/induction F, the polarizability P and the resonance R effects, respectively.

$$-\delta\Delta G^\circ(\mathrm{g}) = \rho_R\sigma_R + \rho_F\sigma_F + \rho_\alpha\sigma_\alpha \tag{16}$$

The left hand side represents the gas phase substituent acidity effect, and ρ_R, ρ_F and ρ_α are reaction constants for

Table IV. Thermodynamic Parameters of Solute at 298 K in GLC for Monosubstituted Benzene Derivatives under Non-polar (1) or Polar (2) Conditions

		$-\Delta\Delta H_s^\circ$ [kJ·mol^{-1}] (1)	$-\Delta\Delta H_s^\circ$ [kJ·mol^{-1}] (2)	$-\Delta\Delta S_s^\circ$ [J·mol^{-1}·K^{-1}] (1)	$-\Delta\Delta S_s^\circ$ [J·mol^{-1}·K^{-1}] (2)	$-\Delta\Delta G_s^\circ$ [kJ·mol^{-1}] (1)	$-\Delta\Delta G_s^\circ$ [kJ·mol^{-1}] (2)
1	Me	6.55±0.27	7.14±0.21	11.66±0.65	13.98±0.54	3.1±0.1	3.0±0.0
2	Et	11.68±0.44	12.81±0.38	20.07±1.09	24.32±1.00	5.7±0.1	5.6±0.1
3	*n*-Pr	16.43±0.52	17.54±0.61	27.46±1.30	32.21±1.55	8.3±0.1	7.9±0.1
4	iso-Pr	14.74±1.13	15.80±0.27	24.72±2.80	29.20±0.67	7.4±0.3	7.1±0.1
5	*n*-Bu	21.52±0.58	22.69±0.82	34.95±1.41	40.23±2.14	11.1±0.2	10.7±0.2
6	iso-Bu	18.63±1.26	20.11±0.44	30.06±3.12	36.29±1.15	9.7±0.3	9.3±0.1
7	*sec*-Bu	18.73±1.22	20.12±0.73	30.31±3.05	36.13±1.88	9.7±0.3	9.4±0.2
8	*tert*-Bu	18.23±0.55	19.17±0.36	29.97±1.36	34.49±0.92	9.3±0.1	8.9±0.1
9	COMe	19.05±1.21	26.42±0.52	30.75±2.97	44.69±1.34	9.9±0.3	13.1±0.1
10	COEt	23.90±1.49	30.16±0.77	37.68±3.70	49.57±1.99	12.9±0.4	15.4±0.2
11	CO_2Me	20.70±1.34	26.92±1.05	33.34±3.29	46.05±2.72	10.8±0.4	13.2±0.2
12	CO_2Et	24.59±1.53	30.29±1.19	39.12±3.79	51.03±3.08	12.9±0.4	15.1±0.3
13	CN	13.90±1.00	22.58±0.61	23.15±2.47	38.35±1.55	7.0±0.3	11.2±0.1
14	NO_2	18.86±1.32	26.73±0.73	29.68±3.25	43.41±1.86	10.0±0.4	13.8±0.2
15	OMe	13.40±0.90	17.67±0.40	22.96±2.22	32.46±1.05	6.6±0.2	8.0±0.1
16	OEt	17.65±1.15	21.33±0.50	29.89±2.83	38.60±1.28	8.7±0.3	9.8±0.1

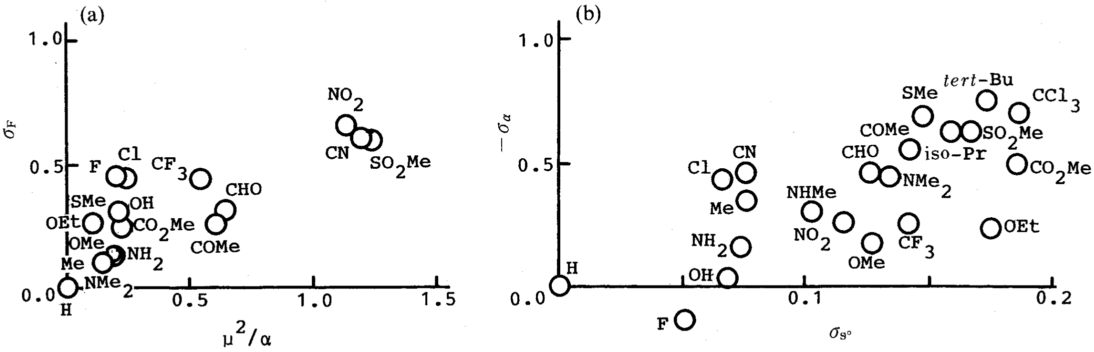

Fig. 4. Plots of σ_F and μ^2/α (a), and σ_α and σ_s° (b) under Non-polar Conditions

the R, F and P effects.

We can determine the chemical meaning of the two descriptors σ_{s° and μ^2/α, since they are related to σ_{s° and σ_α, and μ^2/α and σ_F, respectively.

(1) σ_F and μ^2/α: Figure 4a shows the plots of the data for σ_F and μ^2/α.

The OMe, OEt and CO_2Me groups do not show a linear relationship and this is probably due to the fact that σ_F is determined by the participation of H^+, whereas μ^2/α depends on Ph-R on the wall of the liquid stationary phase. The relationship of these two parameters is given by Eq. 17 below:

$$\sigma_F=0.484(0.155)\mu^2/\alpha+0.058(0.087) \qquad (17)$$

$$n=10, \quad r=0.931, \quad F=52.0, \quad \text{S.D.}=0.094$$

When data on OMe, OEt and CO_2Me are omitted, the regression analysis gives Eq. 17′:

$$\sigma_F=0.539(0.068)\mu^2/\alpha-0.014(0.065) \qquad (17')$$

$$n=7, \quad r=0.994, \quad F=417.5, \quad \text{S.D.}=0.035$$

(2) σ_α and σ_{s°: Figure 4b shows the plots of the data for σ_α and σ_{s°. Regression analysis gives Eq. 18.

$$\sigma_\alpha=-2.441(2.501)\sigma_{s^\circ}-0.088(0.337) \qquad (18)$$

$$n=10, \quad r=0.623, \quad F=5.1, \quad \text{S.D.}=0.189$$

When data on OMe, OEt and CO_2Me are excluded, the following regression Eq. 18′ is obtained.

$$\sigma_\alpha=-3.740(2.034)\sigma_{s^\circ}-0.031(0.247) \qquad (18')$$

$$n=7, \quad r=0.904, \quad F=22.3, \quad \text{S.D.}=0.117$$

These results suggest a favorable correlation between σ_F and μ^2/α, as well as σ_α and σ_{s° except for OMe, OEt and CO_2Me groups, as they are specific to H^+. Thus, we are able to propose that both descriptors for (1) and (2) have the same chemical meaning.

Data on $\Delta\Delta G_s^\circ$ estimated from GLC are analyzed using the substituent parameters σ_F, σ_α and σ_R under non-polar condition, but the result expressed by Eq. 19 was unsatisfactory.

$$-\Delta\Delta G_s^\circ=-9.1(8.6)\sigma_\alpha-0.1(10.0)\sigma_F+16.6(28.0)\sigma_{R^-}+3.9(3.7) \qquad (19)$$

$$n=17, \quad r=0.718, \quad F=4.6, \quad \text{S.D.}=2.5$$

The substituent parameter derived from the equilibria Eq. 16 (which is for the participation of H^+) did not give favorable results.

In comparison with Eq. 19, the regression analyses using σ_{s°, μ^2/α and σ_{R^-} or σ_{s°, σ_F and σ_{R^-} were Eqs. 20 and 21.

$$-\Delta\Delta G_s^\circ=51.5(5.1)\sigma_{s^\circ}+2.3(1.1)\mu^2/\alpha+11.0(5.2)\sigma_{R^-}-0.5(0.8) \qquad (20)$$

$$n=17, \quad r=0.991, \quad F=242.5, \quad \text{S.D.}=0.5$$

$$-\Delta\Delta G_s^\circ=49.5(6.2)\sigma_{s^\circ}+3.1(2.4)\sigma_F+13.3(6.4)\sigma_{R^-}-0.2(1.0) \qquad (21)$$

$$n=17, \quad r=0.986, \quad F=148.3, \quad \text{S.D.}=0.62$$

From Eqs. 19 and 21, when one was the polymer, the descriptor σ_{s° gave better a result than σ_α.

The $\log\gamma$ was proportional to $\Delta\Delta G_s^\circ$ as derived from Eq. 1 and the correlation coefficient r was equal to 0.999. Next, let us discuss the regression analysis of $\log\gamma$ using the descriptors σ_{s°, μ^2/α and σ_R.

Regression Analysis of log γ In our previous report,[16] $\log\gamma$ values of substituted propane and butane were expressed by the linear combination of σ_{s° and μ^2/α. The $\log\gamma$ of mono-substituted benzene derivatives,[8] as well as those of disubstituted benzenes[13] with a delocalization effect, were expressed by the linear combination of σ_π, in addition to σ_{s° and μ^2/α, and we suggested that the additional term σ_π reflects a CH/π interaction[17] between sample and liquid stationary phase.

In this work, we analyzed the $\log\gamma$ values of Table III using σ_{s°, μ^2/α and determined σ_R in the gas phase instead of σ_π. Data on σ_R are linear when plotted the against first vartical ionization potential I_p[18] in Eq. 22.

$$I_p=1.317(0.963)\sigma_{R^+}+5.767(2.246)\sigma_{R^-}-0.285(0.228) \qquad (22)$$

$$n=11,\quad r=0.960,\quad F=41.0,\quad \text{S.D.}=0.187$$

Among the descriptors used in the regression analyses, σ_R is induced only from the chemical equilibrium, but Eq. 22 supports the possibility that I_p could reasonably be substituted by σ_R, although in this work we used σ_R because of the poor experimental data available for I_p.

A similar result was obtained by the regression analysis using four types of descriptors, σ_{s°, μ^2/α and $\sigma_{R^\pm}$.

TABLE V. Descriptors Used in Regression Analyses

		σ_{s°	σ_{R^+}	σ_{R^-}	μ^2/α
1	H	0.000	0.00	0.00	0.000
2	Me	0.076	−0.08	0.00	0.011
3	Et	0.127	−0.08	0.00	0.024
4	*n*-Pr	0.173	−0.08	0.00	0.021
5	iso-Pr	0.159	−0.07	0.00	0.026
6	*n*-Bu	0.213	−0.08	0.00	0.019
7	iso-Bu	0.200	−0.08	0.00	0.019
8	*sec*-Bu	0.202	−0.07	0.00	0.024
9	*tert*-Bu	0.174	−0.07	0.00	0.027
10	COMe	0.142	0.00	0.17	0.602
11	COEt	0.180	0.00	0.17	0.560
12	CO_2Me	0.185	0.00	0.16	0.225
13	CO_2Et	0.219	0.00	0.16	0.203
14	CN	0.076	0.00	0.10	1.185
15	NO_2	0.115	0.00	0.18	1.134
16	OMe	0.127	−0.42	0.00	0.125
17	OEt	0.175	−0.45	0.00	0.110

TABLE VI. Results of Regression Analyses of $\log\gamma$ Values for Mono-substituted Benzene Derivatives at Several Temperatures under Non-polar (1) or Polar (2) Conditions

	$1/T\times10^3$	σ_{s°	σ_{R^+}	σ_{R^-}	μ^2/α	Const.	n	r	F	S.D.
(1)	2.39	4.076		1.078	0.165	−0.062	17	0.988	179.7	0.046
		(0.482)		(0.490)	(0.103)	(0.079)				
	2.42	4.206		1.102	0.173	−0.060	17	0.988	184.2	0.047
		(0.491)		(0.500)	(0.105)	(0.080)				
	2.45	4.363		1.138	0.179	−0.064	17	0.989	186.9	0.048
		(0.505)		(0.514)	(0.108)	(0.083)				
	2.48	4.496		1.180	0.183	−0.065	17	0.989	192.1	0.049
		(0.514)		(0.523)	(0.109)	(0.084)				
	2.51	4.676		1.205	0.191	−0.065	17	0.989	199.8	0.050
		(0.523)		(0.531)	(0.111)	(0.086)				
	2.54	4.837		1.229	0.198	−0.066	17	0.990	203.2	0.051
		(0.535)		(0.544)	(0.114)	(0.088)				
	2.57	4.993		1.242	0.211	−0.067	17	0.990	206.7	0.052
		(0.546)		(0.556)	(0.116)	(0.089)				
(2)	2.39	3.417		2.054	0.338	−0.051	17	0.989	185.2	0.055
		(0.582)		(0.591)	(0.124)	(0.095)				
	2.42	3.588		2.129	0.344	−0.050	17	0.990	203.5	0.054
		(0.575)		(0.584)	(0.122)	(0.094)				
	2.45	3.650	−0.242	2.428	0.350	−0.067	17	0.989	193.9	0.058
		(0.551)	(0.236)	(0.607)	(0.116)	(0.090)				
	2.48	3.808	−0.251	2.500	0.363	−0.066	17	0.989	200.0	0.059
		(0.558)	(0.239)	(0.615)	(0.118)	(0.091)				
	2.51	3.983	−0.259	2.608	0.370	−0.066	17	0.990	203.1	0.061
		(0.575)	(0.246)	(0.633)	(0.121)	(0.093)				
	2.54	4.198	−0.263	2.688	0.380	−0.069	17	0.990	209.1	0.062
		(0.590)	(0.253)	(0.650)	(0.124)	(0.096)				
	2.61	4.501	−0.298	2.813	0.413	−0.069	17	0.990	206.9	0.067
		(0.614)	(0.263)	(0.676)	(0.129)	(0.100)				
	2.68	4.879	−0.335	2.951	0.450	−0.072	17	0.990	205.0	0.072
		(0.643)	(0.275)	(0.708)	(0.136)	(0.104)				
	2.71	5.064	−0.358	3.046	0.466	−0.072	17	0.989	201.0	0.075
		(0.662)	(0.283)	(0.729)	(0.139)	(0.107)				
	2.75	5.235	−0.349	3.110	0.468	−0.071	17	0.990	214.3	0.074
		(0.663)	(0.284)	(0.730)	(0.468)	(0.108)				
	2.79	5.402	−0.393	3.178	0.499	−0.073	17	0.989	199.7	0.079
		(0.686)	(0.294)	(0.756)	(0.145)	(0.111)				

The values in parentheses denote the 95% confidence intervals. *n*, *r*, *F* and S.D. signify the number of data, correlation coefficient, variance ratio and standard deviation, respectively.

Under non-polar conditions at 388 K, Eq. 23 was obtained from the regression analysis of data which are summarized on Table V, using the four types of descriptors;

$$\log\gamma = 5.017(0.582)\sigma_{s^\circ} + 0.007(0.248)\sigma_{\mathrm{R}^+} + 1.208(0.640)\sigma_{\mathrm{R}^-} + 0.214(0.123)\mu^2/\alpha - 0.067(0.095) \quad (23)$$

$$n=17,\quad r=0.990,\quad F=145.1,\quad \mathrm{S.D.}=0.054$$

Here the descriptor σ_{R^+} could be omitted from the 95% confidence level of the regression coeficient, and rewritten as Eq. 24;

$$\log\gamma = 5.013(0.545)\sigma_{s^\circ} + 1.216(0.553)\sigma_{\mathrm{R}^-} + 0.214(0.116)\mu^2/\alpha - 0.068(0.089) \quad (24)$$

$$n=17,\quad r=0.990,\quad F=209.5,\quad \mathrm{S.D.}=0.051$$

Consequently, $\log\gamma$ is indicated by the three types of descriptors, σ_{s°, σ_{R^-} and μ^2/α.

The regression analysis of $\log\gamma$ at several different temperatures are summarized in Table VI.

Furthermore, the regression coefficients of σ_{s°, σ_{R^-} and μ^2/α (a, b and c in Eq. 2) decrease as the measurement temperature increases, and they were found to have a linear relationship *versus* $1/T\times 10^3$, as expressed by Eqs. 25 to 31.

Non-polar Conditions:

$$\text{coefficient,}\quad a = 5.163(0.251)[1/T\times 10^3] - 8.265(0.623) \quad (25)$$

$$n=7,\quad r=0.999,\quad F=2796.5,\quad \mathrm{S.D.}=0.015$$

$$\text{coefficient,}\quad b^- = 0.944(0.153)[1/T\times 10^3] - 1.197(0.379) \quad (26)$$

$$n=7,\quad r=0.990,\quad F=251.8,\quad \mathrm{S.D.}=0.009$$

$$\text{coefficient,}\quad c = 0.238(0.047)[1/T\times 10^3] - 0.402(0.118) \quad (27)$$

$$n=7,\quad r=0.985,\quad F=166.7,\quad \mathrm{S.D.}=0.003$$

Polar Conditions:

$$\text{coefficient,}\quad a = 5.276(0.156)[1/T\times 10^3] - 9.268(0.421) \quad (28)$$

$$n=11,\quad r=0.999,\quad F=5347.00,\quad \mathrm{S.D.}=0.032$$

$$\text{coefficient,}\quad b^+ = -0.427(0.048)[1/T\times 10^3] + 0.811(0.125) \quad (29)$$

$$n=11,\quad r=0.989,\quad F=397.8,\quad \mathrm{S.D.}=0.009$$

$$\text{coefficient,}\quad b^- = 2.236(0.117)[1/T\times 10^3] - 3.033(0.303) \quad (30)$$

$$n=11,\quad r=0.997,\quad F=1854.6,\quad \mathrm{S.D.}=0.023$$

$$\text{coefficient,}\quad c = 0.437(0.027)[1/T\times 10^3] - 0.724(0.078) \quad (31)$$

$$n=11,\quad r=0.997,\quad F=1325.8,\quad \mathrm{S.D.}=0.005$$

According to the classical equation[4)] discribing van der Waals interaction, apparent temperature dependence is only inherent in E_{ori}, but this term is neglected under non-polar conditions.[11)] The temperature dependency of $\log\gamma$ can be obtained from the variation in E_{dis}, E_{rep}, E_{ind}, E_{ori} and E_{CT}, since the intermolecular distance r_{AB} is dependent on temperature. In the next step, we estimated the relative weights of the three effects by means of standard coefficient z-scores. The results, summarized in Table VII, gave the same energy ratio $(E_{\mathrm{dis}}+E_{\mathrm{rep}})/E_{\mathrm{CT}}/(E_{\mathrm{ind}}+E_{\mathrm{ori}})$ at several temperatures. Thus, these results suggest that the temperature-dependency is propotional to r_{AB}. The relative ratios for their energies under non-polar and polar conditions are as follows;

Non-polar Conditions:

$$(E_{\mathrm{dis}}+E_{\mathrm{rep}})/E_{\mathrm{CT}}/(E_{\mathrm{ind}}+E_{\mathrm{ori}}) = 0.83 \gg 0.11 > 0.06 \quad (32)$$

Table VII. Standard Coefficients and Their Ratios of Descriptors σ_{s°, σ_{R^-} and μ^2/α under Non-polar (1) or Polar (2) Conditions

	$1/T\times 10^3$	σ_{s°	σ_{R^+}	σ_{R^-}	μ^2/α	Ratio
(1)	2.39	0.874 (0.103)		0.316 (0.144)	0.238 (0.148)	0.83/0.11/0.06
	2.42	0.875 (0.102)		0.314 (0.142)	0.242 (0.146)	0.83/0.11/0.06
	2.45	0.876 (0.102)		0.313 (0.141)	0.241 (0.145)	0.83/0.11/0.06
	2.48	0.876 (0.100)		0.314 (0.139)	0.239 (0.143)	0.83/0.11/0.06
	2.51	0.879 (0.098)		0.310 (0.137)	0.240 (0.140)	0.83/0.11/0.06
	2.54	0.881 (0.097)		0.306 (0.136)	0.242 (0.139)	0.83/0.11/0.06
	2.57	0.883 (0.097)		0.300 (0.134)	0.250 (0.138)	0.83/0.11/0.06
(2)	2.39	0.599 (0.102)		0.493 (0.142)	0.398 (0.146)	0.47/0.32/0.21
	2.42	0.608 (0.097)		0.493 (0.135)	0.391 (0.139)	0.48/0.32/0.20
	2.45	0.594 (0.090)	−0.093 (0.091)	0.541 (0.135)	0.383 (0.127)	0.44/0.38/0.18
	2.48	0.599 (0.088)	−0.093 (0.089)	0.538 (0.132)	0.383 (0.124)	0.45/0.37/0.18
	2.51	0.603 (0.087)	−0.093 (0.088)	0.540 (0.131)	0.376 (0.123)	0.45/0.37/0.18
	2.54	0.612 (0.086)	−0.091 (0.087)	0.536 (0.130)	0.372 (0.122)	0.46/0.37/0.17
	2.61	0.618 (0.084)	−0.097 (0.085)	0.528 (0.127)	0.381 (0.119)	0.47/0.35/0.18
	2.68	0.626 (0.083)	−0.102 (0.084)	0.518 (0.124)	0.388 (0.117)	0.48/0.35/0.18
	2.71	0.629 (0.082)	−0.105 (0.083)	0.517 (0.124)	0.389 (0.116)	0.48/0.34/0.18
	2.75	0.635 (0.081)	−0.100 (0.081)	0.516 (0.121)	0.381 (0.114)	0.49/0.34/0.18
	2.79	0.635 (0.081)	−0.109 (0.082)	0.511 (0.121)	0.393 (0.114)	0.49/0.33/0.19

The values in parentheses denote the 95% confidence intervals.

Polar Conditions:

$$(E_{\mathrm{dis}}+E_{\mathrm{rep}})/E_{\mathrm{CT}}/(E_{\mathrm{ind}}+E_{\mathrm{ori}}) = 0.47 > 0.35 > 0.18 \quad (33)$$

The contribution of $(E_{\mathrm{dis}}+E_{\mathrm{rep}})$ is dominant under non-polar conditions, and is of a similer magnitude to the sum of E_{CT} and $(E_{\mathrm{ind}}+E_{\mathrm{ori}})$ under polar conditions, and this is consistent with the results from the energy decomposition of the stacking energy of the DNA base pairs studied by M. Aida *et al.*[19)]

$$E_{\mathrm{dis}} > E_{\mathrm{CT}} > E_{\mathrm{ES}} > E_{\mathrm{PL}} \quad (34)$$

There the electrostatic E_{ES} and polarization E_{PL} corresponded to E_{ind} and E_{ori}. They concluded that E_{dis} and E_{CT} made a dominant contribution to the overall stability.

For benzene dimer, P. Hobza *et al.*[20)] used *ab initio* calculations of the sandwich, T-shape and bent structures and concluded that the T-shape was the most stable. E. W. Schlag *et al.*[21)] also arrived at a nearly T-shape structure from the study of IR spectra, since the dihedral angle between the two rings was 70°—80°. When we consider the proportion (Eq. 33) of the three energies of the interaction between DNP and mono-substituted benzene derivatives and the conclusions of the benzene dimer studies, it would be offered that a T- or nearly T-shaped structure is more likely than the stacking (sandwich) structure.

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$E_{\mathrm{ind}} = -(\alpha_{\mathrm{A}}\mu_{\mathrm{B}}^{2}+\alpha_{\mathrm{B}}\mu_{\mathrm{A}}^{2})/r_{\mathrm{AB}}^{6}$

$E_{\mathrm{ori}} = -1/3\boldsymbol{k}T \cdot \mu_{\mathrm{A}}^{2}\mu_{\mathrm{B}}^{2}/r_{\mathrm{AB}}^{6}$

α = polarizability; I = ionization potential; μ = dipole moment; $\boldsymbol{k}$ = Boltzmann constant; r = intermolecular distance.

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