February 2004 *Chem. Pharm. Bull.* **52**(2) 221—225 (2004)

The Interaction of Monosubstituted Benzenes with the Stationary Liquid in Gas Liquid Chromatography

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Received September 10, 2003; accepted December 5, 2003;

In gas liquid chromatography (GLC), the relative retention values log γ was mainly expressed by van der Waals energy (the sum of the dispersion E_{dis} and repulsive E_{rep} energies) to the interactions between monosubstituted benzene derivatives and the nonpolar stationary liquid as squalane. The single exception was that of anilines, and it was corrected by the electrostatic energy (E_{ES}) due to C–H/π hydrogen bond. When the stationary liquid changed from the nonpolar to polar, log γ was estimated by the inductive interaction energy (included in E_{ES}) in addition to the sum of E_{dis} and E_{rep}. In the benzene solution, the relative equilibrium values log K/K_o introduced from the interactions between phenol and substituted benzene derivatives were estimated by E_{ES}. The E_{ES} of $COCH_3$, $CO_2C_2H_5$ groups is especially originated in the excited dipole moments μ_e. The relative frequency values log ν/ν_o derived from O–H or O–D stretching vibration of phenol or methanol-D gave the correlation to E_{ES} as well as log K/K_o. That of anilines–methanol-D however had been out of a linear relation to E_{ES}. The cause is concluded that the aniline–methanol-D is making the proton transfer structure from the discussion about the proton affinity (PA) of the base.

Key words gas liquid chromatography; intermolecular interaction; substituted benzene; electrostatic interaction energy; van der Waals interaction energy

The experimental and theoretical results of hydrogen bonds are presented in many studies. Few of these studies involve the weak hydrogen bond, as it is characterized by molecular recognition in biological response, *etc*. For example, Vargas *et al.*[1] concluded that a weak C_α–H···O=C hydrogen bond in the peptide backbone is enough to play a critical role in the folded structure as collagen triple helix. The geometry of acetylene–ammonia dimer as prototypical C–H···N hydrogen bond was examined by theoretical methods.[2] Hilfiker *et al.*[3] pointed out importance to C–H hydrogen bonding, since there are the dependence on hybridization of the *s* and *p* orbitals of the carbon and on the presence of electron-withdrawing substituents. C–H bond with high *s* character exhibit exceptional acidity, *e.g.* acetylene.[4] This same effect comes from the relatively high acidity of the C–H bonds on cyclopropane (Cp) rings.[5] In other hand, bromocyclopropane (BrCp) with ammonia complex become apparently to form C–H···N hydrogen bond, the proton adjacent to the Br substituent on the Cp ring to the nitrogen of the base.[6] In addition case, the C_{sp^3}–H···N(O) hydrogen bond formed between cyclopentadiene (Cpd) and the nitrogen and oxygen bases is a proton on the sp^3-hybridized carbon that is not adjacent to an electron-withdrawing functional group.[3] They concluded that it is directional rather than no directional and dispersive (van der Waals) interactions.

We discussed the intermolecular interaction of monosubstituted benzenes and the stationary liquid as squalane in the gas liquid chromatography[7,8] (GLC). The interaction of mono-halobenzenes had discussed by Eyring's model[9] and resolved into the physical adsorption.[10] The relative retention values log γ reflected on van der Waals interaction and were estimated by the sum of dispersion (E_{dis}) and repulsion (E_{rep}) energies. On the other hand, the log γ values of monosubstituted benzenes were given by ($E_{\text{dis}}+E_{\text{rep}}$) and inductive energy ($E_{\text{ES}}$). That of aniline however was corrected by the electrostatic energy (E_{ES}) depended on the excited dipole moment μ_e.[8,11—14] In this paper, our GLC data[8] are reinvestigated from the new concept. We also make an attempt at semi-polar stationary liquid as di(*n*-nonyl) phthalate and confirm to be the physical adsorption. This interaction was also the physical adsorption. The O–H···O=C hydrogen bonds of phenol and methylbenzoate *etc.* in solution have settled by E_{ES}, since the regression analyses are carried out using our descriptor σ^*_{bd} estimated from μ_e[13,15] of methylbenzoate *etc.*

Experimental

Relative Retention Value log γ and Experimental Conditions for GLC The log γ define by Eq. 1[16] below.

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

Here $t_R(A)$ and $t_R(B)$ are the retention times of 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 Shimadzu 8A Type gas liquid chromatograph.

Measurement Conditions Sample=monosubstituted benzenes; reference=benzene; mobile phase=nitrogen (N_2); stationary phase=Chromosorb W(AW-DMCS)+20% squalane or 20% di(*n*-nonyl) phathalate (DNP); column temperature=388—418 K, temperature measured to ±0.1 K using a CA thermocouple.

Regression Analysis The regression analyses of the interaction energy change were carried out using the statistical program.[17]

Descriptor for Regression Analyses Descriptor σ_{bd}: Dipole moment of the ground state μ_g: All experimental data are cited from the literature values.[18]

Polarizability α: Polarizability values are given by the Clausius–Mosottie equation, using the observed refractive indices given by the sodium D line at 293 K.[19] The descriptor σ_{bd} is defined by the following equation, and this means electrostatic interaction energy.[20]

$$\sigma_{\text{bd}}=\log[(\mu_g^2/\alpha)(B)/(\mu_g^2/\alpha)(A)] \quad (2)$$

where A and B represent benzene for the reference and its derivatives, respectively. The value μ_g of benzene for reference is 0.31D[21,22] for $\mu_{C_{sp^3}\text{-H}}$. The descriptor σ^*_{bd} derives from the excited dipole moment μ_e and this means an electrostatic energy.

Results and Discussion

Evaluation of Thermodynamic Parameters Data on the temperature-dependence of the relative retention values,

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Table 1. Entropy Changes of Monosubstituted Benzenes-Stationary Interactions in GLC under Nonpolar (Squalane) or Polar (DNP) Conditions and Their Descriptors

	R	$-\Delta\Delta S_s^\circ$ (nonpolar) /J mol^{-1} K^{-1}	$-\Delta\Delta S_s^\circ$ (polar)	σ_M	σ_{bd}
1	H	0.00	0.00	0.000	0.000
2	Me	11.66	13.98	0.072	0.000
3	Et	20.07	24.32	0.133	0.000
4	*n*-Pr	27.46	32.21	0.187	0.000
5	*n*-Bu	34.95	40.23	0.235	0.000
6	OMe	22.96	32.46	0.141	1.144
7	OEt	29.89	38.60	0.194	1.034
8	COMe	30.75	44.69	0.187	1.750
9	COEt	37.68	49.57	0.235	1.711
10	CO_2Me	33.34	46.05	0.241	1.298
11	CO_2Et	39.12	51.03	0.284	1.308
12	CN	23.15	38.35	0.121	2.051
13	NO_2	29.68	43.21	0.198	1.945

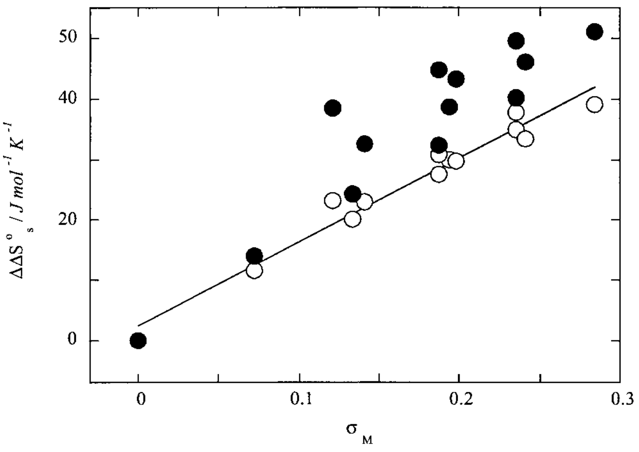

Fig. 1. Correlations between $-\Delta\Delta S_s^\circ$ and the Descriptor σ_M in Monosubstituted Benzenes

○ and ● are nonpolar (squalane) and polar (DNP) conditions.

$\log\gamma$, of monosubstituted benzene derivatives gave a line with a positive slope when plotted against $1/T\times10^3$, and $\Delta\Delta H_s^\circ$ became negative. The $\Delta\Delta H_s^\circ$ is compensatory for $\Delta\Delta S_s^\circ$ and $\Delta\Delta G_s^\circ$ also came out a positive slope when plotted against $\Delta\Delta S_s^\circ$. All the $\Delta\Delta G_s^\circ$ values were smaller than -25 kJ mol^{-1}, and corresponded to the weak intermolecular interactions[7] as the hydrogen bonding. In previous report,[9] the $\Delta\Delta S_s^\circ$ (nonpolar) values estimated from the interaction of the solute (halobenzenes) and nonpolar stationary liquid as squalane, took a good line to activated translational entropy change $\Delta\Delta S^\dagger_{ABC}$ for Eyring's model,[8] since its interaction could be suggested to be the physical adsorption.

It denoted that the interaction brought not on the structure change of the solute and was mainly expressed by E_{dis} and E_{rep}. When we consider the interaction between the gaseous sample (A or B) and the stationary liquid (C=constant in the system), the activated translational entropy change $\Delta\Delta S^\dagger_{ABC}$ for Eyring's adsorption model is expressed in Eq. 2.

$$\Delta\Delta S^\dagger{}_{ABC} = -R[(\ln 2\pi m_B kTe)^{3/2}/h^3 - \ln(2\pi m_A kTe)^{3/2}/h^3]$$
$$= -3/2\,R\ln[2\pi m_B kTe/2\pi m_A kTe] \quad (3)$$

Where R, k, T and h are gas constant, Boltzmann constant, absolute temperature and Plank constant, respectively.

When T is constant, Eq. 3 is given by,

$$\Delta\Delta S^\dagger_{ABC} = -3/2\,R\ln m_B/m_A \quad (4)$$

where m_A and m_B take the relative molecular mass (M_A, M_B) and $\Delta\Delta S^\dagger_{ABC}$ becomes the linear relation to $\ln M_B/M_A$. The $\ln M_B/M_A$ is now replaced with σ_M in following,

$$\ln M_B/M_A = 2.303\log M_B/M_A \equiv \sigma_M \quad (5)$$

The $\Delta\Delta S_s^\circ$ values were relation to σ_M as shown in Fig. 1. The deviation from the line was made the correction for σ_{bd} indicated the inductive interaction. They should be made the distinction for dipole moments of the ground states μ_g[18] for the solute. The regression analyses of the $\Delta\Delta S_s^\circ$ values carry out using σ_M and σ_{bd} as in following,

$$\Delta\Delta S_s^\circ\ (\text{nonpolar}) = 131.79(7.44)\sigma_M + 1.62(0.69)\sigma_{bd} + 2.01(1.28) \quad (6)$$
$$n=13,\ r=0.988,\ F=211.0,\ \text{S.D.}=1.82$$

where σ_M and σ_{bd} denote E_{dis} and E_{rep}, and electrostatic energy (E_{ES}) between the solute and stationary liquid. This result was signified that the gaseous solute is not converted the molecular structure except for aniline into the measurable reaction time as in GLC.

We also discuss on $\Delta\Delta S_s^\circ$ (polar) under polar condition as DNP having aromatic ring.

$$\Delta\Delta S_s^\circ\ (\text{polar}) = 147.67(9.39)\sigma_M + 6.71(0.88)\sigma_{bd} + 3.35(1.61) \quad (7)$$
$$n=13,\ r=0.990,\ F=241.5,\ \text{S.D.}=2.30$$

The coefficient of descriptor σ_M of Eq. 7 was coincided with the limits of the error to Eq. 6, but that of σ_{bd} was large. As this stationary liquid (DNP) was more polar than squalane, the contribution of the electrostatic interaction increased. It was suggested that the interaction between and DNP coincided of π/π stacking by Sinnokrot *et al.*[23] They concluded that the variation of binding energies for face-to-face dimers of benzene with substituted benzenes corresponded to both electrostatic and dispersion interactions. Our descriptors σ_M and σ_{bd} are, therefore, determined on the dispersion and electrostatic interaction energies. Our method is classical but estimated coefficients of the descriptors reflect each contribution.

The regression analysis of the $\log\gamma$ values (1—17) except for anilines in Table 2 was given by,

$$\log\gamma = 3.802(0.195)\sigma_M + 0.102(0.017)\sigma_{bd} + 0.009(0.038) \quad (8)$$
$$n=17,\ r=0.985,\ F=234.8,\ \text{S.D.}=0.055$$

The regression analysis included anilines is given by using σ^*_{bd}, this is derived from μ_e (8.13D)[14] of the singlet excited states for twisted intramolecular CT (TICT) states [$n-\pi^*$] as in aniline.

$$\log\gamma = 3.653(0.172)\sigma_M + 0.125(0.011)\sigma^*_{bd} + 0.026(0.035) \quad (9)$$
$$n=22,\ =0.985,\ F=300.7,\ \text{S.D.}=0.056$$

Although TICT states of aniline have not reported experimentally, Honda *et al.* pointed out to be able existence. Our result suggested that the TICT states of aniline have actually recognized from the discussion of μ_e in GLC. We think that the interaction of aniline–squalane is due to CH/π between CH of squalane and increased π electron density on benzene ring by intramolecular CT. Intermolecular interaction in gas phase had been analyzed by using our descriptors σ_M and

Table 2. Relative Retention Values log γ of Monosubstituted Benzenes under Nonpolar (Squalane) Condition and Their Descriptors

	R	log γ	σ_M	σ_{bd}	σ^*_{bd}
1	H	0.000	0.000	0.000	0.000
2	Me	0.301	0.072	0.000	0.000
3	Et	0.538	0.133	0.000	0.000
4	*n*-Pr	0.760	0.187	0.000	0.000
5	*i*-Pr	0.684	0.187	0.000	0.000
6	*n*-Bu	1.007	0.235	0.000	0.000
7	*i*-Bu	0.895	0.235	0.000	0.000
8	*s*-Bu	0.896	0.235	0.000	0.000
9	*t*-Bu	0.853	0.235	0.000	0.000
10	OMe	0.595	0.141	1.144	1.144
11	OEt	0.781	0.194	1.034	1.034
12	COMe	0.940	0.187	1.750	1.750
13	COEt	1.169	0.235	1.711	1.711
14	CO_2Me	1.003	0.241	1.298	1.298
15	CO_2Et	1.179	0.284	1.308	1.308
16	CN	0.684	0.121	2.051	2.051
17	NO_2	0.977	0.198	1.945	1.945
18	NH_2	0.670	0.076	1.296	2.77[a]
19	NHMe	0.939	0.137	1.333	2.70[a]
20	NMe_2	1.051	0.191	1.237	2.64[a]
21	NHEt	1.104	0.191	1.284	2.65[a]
22	NEt_2	1.340	0.281	1.249	2.55[a]

a) is modified from the excited dipole moment $\mu_{e,NH_2}=8.13D$.[14]

σ_{bd} as the dispersion and electrostatic interaction energies. We developed an analysis using our descriptors to the frequency and its estimated equilibrium constant in the solution.

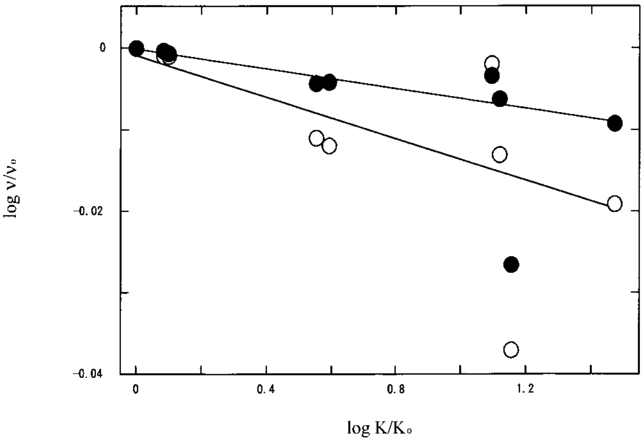

Fig. 2. Correlations between log K/K_o Values and log ν/ν_o Values for Substituted Benzenes with Phenol in CCl_4 (○) and with Methanol-D in Benzene (●) Solutions

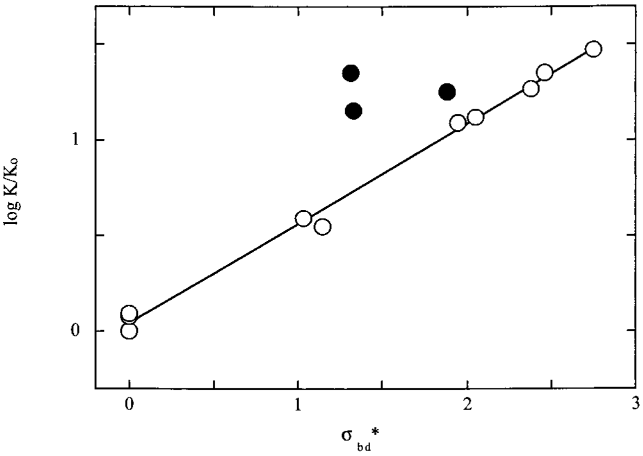

Fig. 3. Correlation between log K/K_o and the Descriptor σ^*_{bd}

Hydrogen Bonds for Substituted Benzene Derivatives with Phenol in CCl_4 Fujii *et al.*[24] observed infrared–ultraviolet double resonance spectroscopy for the neutral ground state of phenol–benzene cluster. They concluded as follows: A small low-frequency shift of the OH vibration of the phenol site was reflected in the π-hydrogen bonded structure. This structure suggested that both the π-hydrogen bonds have been the O–H and the C–H bond at the ortho position of the phenol site to a part of the benzene ring. This structure was also the unique π-hydrogen bonded structure in the B3LYP/6-31G(*d*,*p*) level calculations. The OH frequency shifts were smaller than those in the σ-type hydrogen bonds and those expected from the proton affinity (PA) of benzene.[25] It was suggested that the origin of the abnormal might be the C–H/π hydrogen bond in phenol–benzene. The interaction in benzonitrile–phenol was determined to have a linear σ-type hydrogen bonded structure.[26] The hydrogen bonding study of phenol–amines[27] was performed with *ab initio* calculation at RMP2/6—311++g** level using (U)B3LYP/6—31+g* geometries, since they were depended on the basicity of amines. That is, they concluded as following, when PA of amines is larger than *ca.* 204 kcal mol^{-1}, it was predominantly the proton transfer. The range of *ca.* 190—197 kcal mol^{-1} caused both the proton transfer and nonproton transfer structures were found to be energy minima. When PA of the amines is smaller than *ca.* 189 kcal mol^{-1}, there was no proton transfer form. In our analyzed series according to their conclusion, benzene derivatives are in general made no proton transfer structures but we are expected proton transfer structure only aniline as the PA of aniline is 209.1 kcal mol^{-1}.[28] The ν and K are expressed the OH stretching vibration and the equilibrium constant estimated by ν in the 1 : 1 complex between benzenes and phenol.[29] We were introduced the relative values, log K/K_o and log ν/ν_o, modified from K and ν as shown in Eq. 8,

$$\log K/K_o=\log K_B/K_A, \quad \log \nu/\nu^a_o=\log \nu_B/\nu_A \qquad (10)$$

where A and B represent benzene for the reference and its derivatives, respectively. The relation to log ν/ν^a_o and log K/K_o values was on a line except for aniline as shown in Fig. 2. The log ν/ν^a_o of aniline–phenol is included in the influence of the proton transfer at the local binding site. It is a point of difference between K and ν, when the quantity of the proton transfer is very small, and K and ν values may be given the different information in the same system. When the log K/K_o values plotted on σ_{bd}, those of NH_2, COMe, CO_2Et *etc.* were out of the line as shown in Fig. 3. In previous report,[12] the plot of aniline was moved on the line by σ^*_{bd} introduced from μ_e instead of σ^*_{bd}. We think now that the above result was wrong, because it was a coincidence on the line. For COR, CO_2R *etc.*, they are shifted also on the line to σ^*_{bd}[12,13] (Fig. 3). The regression analysis of log K/K_o is given by,

$$\log K/K_o=0.520(0.014)\sigma^*_{bd}+0.049(0.024) \qquad (11)$$

$n=10$ (H, Me, Et, OMe, OEt, NO_2, CN, COMe, CO_2Et, 1,4-NO_2, CO_2Et),
$r=0.997$, $F=1369.4$, S.D.$=0.046$

This result suggests that the hydrogen bonding structure

Table 3. Log K/K_o and log ν/ν_o^a Values for Phenol and log ν/ν_o^b Values for Methanol-D with Substituted Benzenes and Their Descriptors

	R	log K/K_o	log ν/ν_o^a	log ν/ν_o^b	σ_{bd}	σ^*_{bd}
1	H	0.000	0.0000	0.0000	0.000	0.000
2	Me	0.084	−0.0010	−0.0003	0.000	0.000
3	Et	0.097	−0.0010	−0.0007	0.000	0.000
4	OMe	0.553	−0.0110	−0.0043	1.144	1.144
5	OEt	0.594	−0.0120	−0.0041	1.034	1.034
6	NH_2	1.155	−0.0370	−0.0265	1.327	2.77[a)]
7	NO_2	1.097	−0.0020	−0.0034	1.945	1.40[b)]
8	CN	1.121	−0.0130	−0.0062	2.051	2.051
9	COMe	1.472	−0.0190	−0.0092	1.750	2.75[a)]
10	CO_2Et	1.359	−0.0070	—	1.308	2.46[a)]
11	1,4-NO_2, CO_2Et	1.269	−0.0130	—	1.880	2.38[a)]
12	$CH{=}CH_2$	—	—	−0.0003	0.000	0.000
13	NHMe	—	—	−0.0253	1.310	2.70[a)]
14	NMe_2	—	—	−0.0248	1.240	2.64[a)]

a or b values were estimated by O–H or O–D bound stretching vibrations of phenol or methanol-D. *a*) is modified from the excited dipole moment $\mu_{e,NH_2}=8.13$D and $\mu_{e,COMe}=8.0$D and $\mu_{e,CO_2Et}=6.7$D. *b*) is estimated from the twisted NO_2 group.[34—36)]

arises from the twisted oxygen in comparison with section 1. The log K/K_o values of acetophenone and ethylbenzoate were estimated by E_{ES}.

Hydrogen Bonding for Monosubstituted Benzenes with Methanol-D in Benzene The ν_{OD} values were presented by Kagiya *et al.*[30)] who had been measured O–D vibrational band of methanol-D with monosubstituted benzene derivatives in benzene. Methanol–benzene was estimated by using a time-of-flight mass (TOFMass) spectrometer to be OH/π type hydrogen bond structure as well as phenol.[31,32)] Methanol–benzonitrile[26)] was determined to be perpendicularly CN triple bond (π-type) as differed from phenol. In our analyzed data, log ν/ν_o^b (MeOD) values are good linear relationship with log ν/ν_o^a (PhOH) as the correlation coefficient is 0.962. We think to be the OD/π type hydrogen bonding structure as well as that of phenol. The dominant products of pyrimidine–methanol[33)] were confirmed $C_4H_4N_2H^+$ and CH_3O from a fast proton transfer reaction by using TOFMass. The PA values of pyrimidine and aniline are 215.80 kcal mol^{-1} and 209.1 kcal mol^{-1}, respectively. The hydrogen bonding of aniline–methanol-D is also possibility to produce $C_6H_5NH_2D^+$ and CH_3O. The regression analysis omitted anilines is given by,

$$\log \nu/\nu_o^b = -0.0032(0.0005)\sigma^*_{bd} - 0.0006(0.0008) \qquad (12)$$

$n=9$ (H, Me, Et, OMe, OEt, NO_2, CN, COMe, $CH{=}CH_2$),
$r=0.986$, $F=246.60$, S.D.$=0.0006$

The result suggests that the OD/π type hydrogen bonding is corresponded to σ^*_{bd} except for anilines and so-called, it is E_{ES} depended on μ_e at the reaction site. That is, log ν/ν_o values were mainly fixed on E_{ES} in nonpolar solution as shown in Fig. 2. As the log ν/ν_o^b value of the aniline on binding site is contained the influence of the protonation, it is not determined only by E_{ES}.

Conclusions

The interaction between the solute and polar stationary phase has expressed by the E_{ES} depended on σ_{bd} derived from their μ_g in addition to E_{dis} and E_{rep}. They are also the physical adsorption, since the structures of their solutes do not change. In nonpolar solution, the log K/K_o values of substituted benzenes with phenol are estimated by E_{ES} evaluated to the σ^*_{bd} derived from μ_e of acetophenone and methyl benzoate. But the log ν/ν_o^b values of anilines with methanol-D are not decided in only E_{ES}, since it is suggested to reflect the protonation in the binding site as nitrogen of anilines. We have not yet presented the valuated descriptor estimated the protonation in solution.

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Induction and orientation interaction energies are following equations;

$$E_{ind} = -(\alpha_A\mu_B^2 + \alpha_B\mu_A^2)/r_{AB}^6$$

$$E_{ori} = -1/3kT\mu^2{}_A\mu^2{}_B/r^6_{AB}$$

where α, μ, k and r are polarizability, dipole moment, Boltzmann constant and intermolecular distance, respectively. As r_{AB}^6 equals $\alpha_A\alpha_B$, and both E_{ind} and E_{ori} are relation to μ_B^2/α_B due to constant A. σ_{bd} is

the descriptor of both.
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