[Chem. Pharm. Bull.
33(8)3385—3389(1985)]

Studies on the Specific Retention Ratio in Gas-Liquid Chromatography of Acyclic Saturated Hydrocarbons by Means of Lennard-Jones (12,6) Potential Force Constants

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(Received December 24, 1984)

Many unknown Lennard-Jones (12,6) potential force constants ε/k [K] of acyclic saturated hydrocarbons could be estimated from the linear relationship between known ε/k [K] (determined from the combined viscosity and 2nd virial coefficient data) and S°_{298} (g).

The dispersion interaction term $E_{\text{dis.}}$ in gas-liquid chromatography (GLC) can be determined by using the mixture rule as the difference of $-2\,[\varepsilon_{ii}\varepsilon_{jj}]^{1/2}$ for the solute–stationary phase and solute–mobile phase pairs. Parameter $\varepsilon_{ii}{}^{1/2}\times 10^{-8}$ $\text{erg}^{1/2}$ is linearly related to $\log\gamma$ measured by GLC of acyclic saturated hydrocarbons under apolar conditions.

The correlation between $\log\gamma$ and S°_{298} (g), as well as that of $\log\gamma$ against $E_{\text{dis.}}$, supports the dependencies of $E_{\text{dis.}}$ and $\Delta H^\circ_{\text{s}}$ (enthalpy of dissolution) on S°_{298} (g).

Keywords——gas-liquid chromatography; specific retention ratio; Lennard-Jones (12,6) potential; dispersion force; standard entropy S°_{298} (g)

Many retention data in the field of gas-liquid chromatography (GLC) have been accumulated,[1,2] affording useful information for both qualitative and quantitative chemical analyses.

However, the chemical meaning of retention data based on molecular theory has not yet been fully elucidated.

In our previous communication,[3] the specific retention ratio of acyclic saturated hydrocarbons was shown to be correlated with the gaseous standard entropies S°_{298} (g),[4] but the chemical significance of this has not yet been resolved. This paper deals with an evaluation of the above evidence in terms of the Lennard-Jones (12, 6) potential force constant.

Experimental

Regression Analysis——Regression analyses were carried out using an ACOS 1000 computer at the Computation Center of Osaka University and a PC-9801 personal computer utilizing a library program (NEC TSS library TSS/LIB-6) and a program written by us in BASIC.

The standard deviation (S.D.) is given by $\text{S.D.}=[Se/(n-k-1)]^{1/2}$, where n and k mean the numbers of observations and variables, respectively, and Se denotes the sum of squares of residuals.

Results and Discussion

Evaluation of the Dispersion Force between Apolar Unlike Pairs by Means of Lennard-Jones (12, 6) Potential Force Constant ε/k [K]

Based on molecular theory, the specific retention ratio in GLC of acyclic saturated hydrocarbons using apolar stationary and mobile phases can be intuitively ascribed to the dispersion interaction between the solute and stationary phase, as well as the mobile phase.

The contribution of the dispersion interaction $E_{\mathrm{dis.}}$ can be expressed by Eq. 1 given by London[5];

$$E_{\mathrm{dis}} = -(3/2)[\alpha_1\alpha_2/r_{12}{}^6][I_1I_2/(I_1+I_2)] \tag{1}$$

where

α_1, α_2 = polarizability $\times 10^{-24}$ [cm^3] of 1 and 2

r_{12} = separation $\times 10^{-8}$ [cm] of 1 and 2

I_1, I_2 = ionization potential [eV] of 1 and 2

Unfortunately, when 1 or 2 has a nonspherical flexible molecular framework, Eq. 1 does not hold, because r_{12} takes a statistical mean value, and $E_{\mathrm{dis.}}$ becomes unreliable.

This situation prompted us to utilize the Lennard-Jones (12, 6) potential given by Eq. 2, and its force constant.

For a like pair, Eq. 2 applies;

$$\phi = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6] \tag{2}$$

where $\sigma = r_\circ(1/2)^{1/6}$, effective diameter of the molecule $\times 10^{-8}$ [cm], $r_\circ$ = separation of the molecule at potential minimum $\times 10^{-8}$ [cm], ε = minimum potential $\times 10^{-16}$ [erg].

In Eq. 2, the first term represents a repulsive force, and the second denotes an attractive one, corresponding to the $E_{\mathrm{dis.}}$ of an apolar pair, and this equation can be extended to an unlike pair, using a mixture rule as below;

$$\sigma_{12} = 1/2(\sigma_{11}+\sigma_{22})$$

$$r_{\circ 12} = 1/2(r_{\circ 11}+r_{\circ 22})$$

$$\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})$$

Consequently, at the potential minimum of an apolar unlike pair, $E_{\mathrm{dis.}}$ could be given by Eq. 3;

$$\begin{aligned} E_{\mathrm{dis.}} &= -4\sigma_{12}(\varepsilon_{12}/r_{\circ 12})^6 \\ &= -4(\varepsilon_{11}\varepsilon_{22})^{1/2}[(\sigma_{11}+\sigma_{22})/(r_{\circ 11}+r_{\circ 22})]^6 \\ &= -4(\varepsilon_{11}\varepsilon_{22})^{1/2}[\{r_{\circ 11}(1/2)^{1/6}+r_{\circ 22}(1/2)^{1/6}\}/(r_{\circ 11}+r_{\circ 22})]^6 \\ &= -2(\varepsilon_{11}\varepsilon_{22})^{1/2} \end{aligned} \tag{3}$$

When ε_{11} and ε_{22} refer to the solute and specified stationary phase, respectively, $E_{\mathrm{dis.}}(1, 2)$ becomes proportional to $\varepsilon_{11}{}^{1/2}$. In a similar way, $E_{\mathrm{dis.}}$ given by the interaction between the solute and the specified mobile phase having ε_{33}, $E_{\mathrm{dis.}}(1, 3)$ can be given by Eq. 4,

$$E_{\mathrm{dis.}}(1,3) = -2(\varepsilon_{11}\varepsilon_{33})^{1/2} \tag{4}$$

From Eqs. 3 and 4, Eq. 5 may derived.

$$E_{\mathrm{dis.}}(1,2) - E_{\mathrm{dis.}}(1,3) = -2\varepsilon_{11}{}^{1/2}(\varepsilon_{22}{}^{1/2} - \varepsilon_{33}{}^{1/2}) \propto \varepsilon_{11}{}^{1/2} \tag{5}$$

Selection and Estimation of the Lennard-Jones (12, 6) Potential Force Constant ε/k [K]

Hitherto, numerous kinds of force constants ε/k [K] of the Lennard-Jones (12, 6) potential, based on gas viscosity or the second virial coefficient, have been accumulated and summarized,[6,7] but, unfortunately, they show a tremendous scatter and we could not select reliable values. Nevertheless, the values of ε/k [K] determined from the combined viscosity

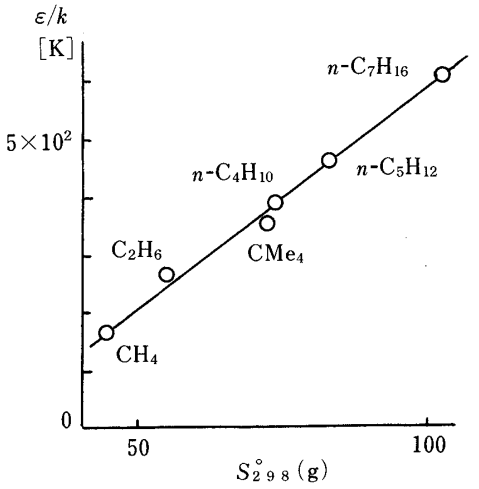

Fig. 1. Correlation between ε/k [K] of Apolar Saturated Hydrocarbons and S°_{298} (g)

and 2nd virial coefficient data were revealed to be linearly related to S°_{298}(g) among apolar aliphatic hydrocarbons,[8] as shown in Fig. 1.

Regression analysis of the data points gives Eq. 6; the unknown values of ε/k [K] summarized in Table I have been determined by inter- or extrapolation,

$$\varepsilon/k[\mathrm{K}]=7.574\,S^\circ_{298}(\mathrm{g})-163.594 \qquad (6)$$
$$(\pm 1.359) \quad (\pm 101.22)$$

$$r=0.992,\ \mathrm{S.D.}=22.616,\ F=239.4,\ d=3.02$$

Correlation between Specific Retention Ratio γ of Acyclic Saturated Hydrocarbons Determined under Apolar Conditions and Force Constant ε/k [K] of the Lennard-Jones (12, 6) Potential

All the values of S°_{298}(g), two kinds of specific retention data, force constant ε/k [K] and the parameter $\varepsilon_{11}{}^{1/2}$ estimated by Eq. 6 are summarized in Table I.

As shown by Eq. 7, the values of log γ are linearly related to $\varepsilon_{11}{}^{1/2}\times 10^{-8}$ erg$^{1/2}$ of the solutes.

$$\log\gamma=0.2354\,\varepsilon_{11}{}^{1/2}[10^{-8}\,\mathrm{erg}^{1/2}]-6.3280 \qquad (7)$$
$$(\pm 0.012) \qquad (\pm 0.3364)$$

$$r=0.986,\ \mathrm{S.D.}=0.1328,\ F=1561.49,\ d=1.83$$

This result supports the dependency of log γ on the dispersion interaction $E_{\mathrm{dis.}}$ derived from the force constant ε/k [K] of the Lennard-Jones (12, 6) potential determined from the combined viscosity and 2nd virial coefficient data, together with the mixture rule.

Chemical Meaning of the Linear Relation between log γ and $\varepsilon_{11}{}^{1/2}$

The total molecular interaction energies given by GLC can be expressed by Eq. 8,

$$\Delta E_{\mathrm{total}}=E_{12}-E_{13} \qquad (8)$$

where the subscripts 1, 2 and 3 mean the solute, stationary phase and mobile phase, and 12 and 13 denote the solute–stationary phase and solute–mobile phase interactions. Consequently, the energy determining the magnitude of the retention data should be approximated to $E_{12}-E_{13}$ as below;

$$\begin{aligned}\Delta E_{\mathrm{total}}&=E_{12}-E_{13}\\&=E_{\mathrm{dis.}}(12)-E_{\mathrm{dis.}}(13)\\&=-2\varepsilon_{11}{}^{1/2}(\varepsilon_{22}{}^{1/2}-\varepsilon_{33}{}^{1/2})\end{aligned}$$

TABLE I. S°_{298} (g)[4] [cal mol^{-1} deg^{-1}], Retention Data γ and $\log\gamma$,[2] Force Constant ε/k [°K] and Parameter $\varepsilon^{1/2}\times10^{-8}$ [erg$^{1/2}$]

	S°_{298} (g)	γ	$\log\gamma$	ε/k	$\varepsilon^{1/2}$
1. C_1	44.52	0.005	−2.3	166.78	15.171
2. C_2	54.85	0.01	−2.0	274.48	19.462
3. C_3	64.51	0.03	−1.52	324.97±27.99	21.177
4. C_4	74.12	0.11	−0.96	398.92	23.463
5. C_5	83.94	0.35	−0.46	474.15	25.580
6. C_6	92.83	1.00	0.00	539.46±40.17	27.285
7. C_7	102.27	2.82	0.45	621.23	29.280
8. C_8	111.55	7.66	0.88	681.23±64.14	30.661
9. 2-Me-C_3	70.42	0.07	−1.15	369.73±25.75	22.588
10. 2-Me-C_4	82.12	0.26	−0.59	458.34±29.69	25.150
11. 2-Me-C_5	90.95	0.72	−0.14	525.22±38.06	26.922
12. 3-Me-C_5	90.97	0.84	−0.08	525.37±38.08	26.926
13. 2-Me-C_6	100.38	2.02	0.31	596.64±49.35	28.694
14. 3-Me-C_6	101.37	2.19	0.34	604.13±50.61	28.874
15. 2-Me-C_7	108.81	5.46	0.74	660.48±60.42	30.190
16. 4-Me-C_7	108.35	5.53	0.74	657.00±59.80	30.111
17. 3-Me-C_7	110.32	5.85	0.77	671.92±62.47	30.451
18. 2,2-Me_2-C_3	73.23	0.13	−0.89	357.13	22.200
19. 2,2-Me_2-C_4	85.62	0.51	−0.29	484.85±32.63	25.867
20. 2,3-Me_2-C_4	87.42	0.69	−0.16	498.48±34.36	26.228
21. 2,2-Me_2-C_5	93.90	1.28	0.11	547.56±41.41	27.489
22. 2,4-Me_2-C_5	94.80	1.37	0.14	554.38±42.47	27.659
23. 3,3-Me_2-C_5	95.93	1.75	0.24	562.93±43.82	27.872
24. 2,3-Me_2-C_5	98.96	2.02	0.31	585.88±47.55	28.434
25. 2,2-Me_2-C_6	103.06	3.49	0.54	616.93±52.80	29.178
26. 2,5-Me_2-C_6	104.96	3.87	0.59	631.32±55.29	29.517
27. 2,4-Me_2-C_6	106.51	3.93	0.59	643.06±57.34	29.790
28. 3,3-Me_2-C_6	104.70	4.14	0.62	629.35±54.94	29.474
29. 2,3-Me_2-C_6	106.11	5.09	0.71	640.03±56.81	29.719
30. 3,4-Me_2-C_6	107.15	5.53	0.74	647.91±58.20	29.902
31. 2,2-Me_2-C_7	113.07	9.16	0.96	692.74±66.22	30.919
32. 2,2,3-Me_3-C_4	91.61	1.43	0.16	530.22±38.79	27.050
33. 2,2,4-Me_3-C_5	101.15	2.48	0.39	602.47±50.33	28.834
34. 2,2,3-Me_3-C_5	101.62	3.81	0.58	606.03±50.93	28.919
35. 2,3,4-Me_3-C_5	102.31	4.49	0.65	611.25±51.82	29.044
36. 2,3,3-Me_3-C_5	103.14	4.61	0.66	617.54±52.90	29.193
37. 2,2,5-Me_3-C_5	103.14	4.61	0.66	617.54±52.90	29.193
38. 2,2,4-Me_3-C_6	111.34	6.76	0.83	679.64±63.85	30.625
39. 2,4,4-Me_3-C_6	112.14	7.86	0.90	685.70±64.95	30.761
40. 2,3,5-Me_3-C_6	112.30	8.75	0.94	686.91±65.17	30.789
41. 2,2,3-Me_3-C_6	111.34	9.28	0.97	679.64±63.85	30.625
42. 3-Et-C_5	98.35	2.43	0.39	581.26±46.79	28.322
43. 3-Et-2-Me-C_5	105.43	5.09	0.71	634.88±55.91	29.600
44. 3-Et-3-Me-C_5	103.48	5.40	0.73	620.11±53.34	29.253
45. 3-Et-C_6	109.51	5.88	0.77	665.78±61.37	30.311
46. 3-Et-2,2-Me_2-C_5	109.96	8.91	0.95	669.19±61.98	30.389
47. 2,2,3-Me_3-C_5	108.23	8.49	0.93	656.09±59.64	30.090
48. 2,2,4,4-Me_4-C_5	101.13	5.53	0.74	602.32±50.31	28.831

When both stationary and mobile phases are specified, the term in the bracket becomes constant, and ΔE_{total} is proportional to ${\varepsilon_{11}}^{1/2}$, as given by Eq. 9;

$$\Delta E_{\text{total}} \propto {\varepsilon_{11}}^{1/2} \qquad (9)$$

On the other hand, from the chemical thermodynamics of GLC, log γ—the logarithm of the specific retention ratio—can be expressed by Eq. 10;

$$\log\gamma = \log V_g(\mathrm{HC}) - \log V_g(n\text{-hexane}) = -\frac{\Delta H_s(\mathrm{HC})^\circ - \Delta H_s(n\text{-hexane})^\circ}{RT} \qquad (10)^{9)}$$

where $\log V_g = -\Delta H_s^\circ/RT$, and ΔH_s° denotes the enthalpy of dissolution.

Thus, the linear relation between log γ and $\varepsilon_{11}{}^{1/2}$ suggests that the enthalpy of dissolution ΔH_s° arises from the dispersion interaction, and, moreover, the correlation between $S_{298}^\circ(\mathrm{g})$ and log γ described in our previous communication$^{3)}$ also supports the dependencies of $E_{\mathrm{dis.}}$ and ΔH_s° on $S_{298}^\circ(\mathrm{g})$.

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