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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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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_{dis} in gas-liquid chromatography (GLC) can be determined by using the mixture rule as the difference of $-2 [\epsilon_{ii}\epsilon_{jj}]^{1/2}$ for the solute-stationary phase and solute-mobile phase pairs. Parameter $\epsilon_{ii}^{1/2} \times 10^{-8}$ 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_{dis} , supports the dependencies of E_{dis} and ΔH_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 $\text{S.D.} = [\text{Se}/(n-k-1)]^{1/2}$, 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 $E_{\text{dis.}}$ can be expressed by Eq. 1 given by London⁵;

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

where

α_1, α_2 = polarizability $\times 10^{-24}$ [cm³] 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 $E_{\text{dis.}}$ 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;

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

where $\sigma = r_o(1/2)^{1/6}$, effective diameter of the molecule $\times 10^{-8}$ [cm], r_o = 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 $E_{\text{dis.}}$ of an apolar pair, and this equation can be extended to an unlike pair, using a mixture rule as below;

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

$$r_{o12} = 1/2(r_{o11} + r_{o22})$$

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

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

$$\begin{aligned} E_{\text{dis.}} &= -4\sigma_{12}(\epsilon_{12}/r_{o12})^6 \\ &= -4(\epsilon_{11}\epsilon_{22})^{1/2}[(\sigma_{11} + \sigma_{22})/(r_{o11} + r_{o22})]^6 \\ &= -4(\epsilon_{11}\epsilon_{22})^{1/2}[(r_{o11}(1/2)^{1/6} + r_{o22}(1/2)^{1/6})/(r_{o11} + r_{o22})]^6 \\ &= -2(\epsilon_{11}\epsilon_{22})^{1/2} \end{aligned} \quad (3)$$

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

$$E_{\text{dis.}}(1, 3) = -2(\epsilon_{11}\epsilon_{33})^{1/2} \quad (4)$$

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

$$E_{\text{dis.}}(1, 2) - E_{\text{dis.}}(1, 3) = -2\epsilon_{11}^{1/2}(\epsilon_{22}^{1/2} - \epsilon_{33}^{1/2}) \propto \epsilon_{11}^{1/2} \quad (5)$$

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,

$$\epsilon/k[\text{K}] = 7.574 S_{298}^\circ(\text{g}) - 163.594 \quad (6)$$

(± 1.359) (± 101.22)

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

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 $\epsilon_{11}^{1/2}$ estimated by Eq. 6 are summarized in Table I.

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

$$\log \gamma = 0.2354 \epsilon_{11}^{1/2} [10^{-8} \text{ erg}^{1/2}] - 6.3280 \quad (7)$$

(± 0.012) (± 0.3364)

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

This result supports the dependency of $\log \gamma$ on the dispersion interaction E_{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 $\log \gamma$ and $\epsilon_{11}^{1/2}$

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

$$\Delta E_{\text{total}} = E_{12} - E_{13} \quad (8)$$

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;

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

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 $\epsilon^{1/2} \times 10^{-8}$ [erg^{1/2}]

	S_{298}° (g)	γ	$\log \gamma$	ϵ/k	$\epsilon^{1/2}$
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 $\epsilon_{11}^{1/2}$, as given by Eq. 9;

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

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

$$\begin{aligned} \log \gamma &= \log V_g(\text{HC}) - \log V_g(n\text{-hexane}) \\ &= -\frac{\Delta H_s(\text{HC})^\circ - \Delta H_s(n\text{-hexane})^\circ}{RT} \end{aligned} \quad (10)^9$$

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

Thus, the linear relation between $\log \gamma$ and $\varepsilon_{11}^{1/2}$ suggests that the enthalpy of dissolution ΔH_s° arises from the dispersion interaction, and, moreover, the correlation between $S_{298}^\circ(\text{g})$ and $\log \gamma$ described in our previous communication³⁾ also supports the dependencies of E_{dis} and ΔH_s° on $S_{298}^\circ(\text{g})$.

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