

Thermodynamic properties of rigid polycyclic molecules (2) Partial molar volumes of polycyclic aromatics compared with the RISM integral equation theory

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Abstract

Partial molar volumes of polycyclic aromatics (benzene, naphthalene, anthracene, phenanthrene, chrysene, diphenyl, *o*-, *m*-, *p*-terphenyl) at infinite dilution were measured. The additivity rule with respect to the number of aromatic rings holds very accurately for the set of solute molecules of benzene, naphthalene and phenanthrene, as well as the set of benzene, diphenyl, and *p*-terphenyl. The linearity of the set of data of benzene, naphthalene and anthracene is slightly worse. The fact that the additivity rule holds including monomer for these series of polycyclic aromatics makes a sharp contrast with the case of *n*-alkane, where the partial molar volume of methane is somewhat larger than the value expected from the additivity rule. In order to explore the origin of this difference, theoretical calculations were made for model chain molecules. The calculated result suggests that this difference between polycyclic aromatics and *n*-alkane is not caused by the size difference between monomer and solvent molecule. The partial molar volume of isomers of terphenyl becomes smaller as the molecule takes more stretched form, which is quite opposite to many other compounds. This peculiar behavior is referred to the increase of dihedral angle between two aromatic rings along with the decrease of bond angle. © 1997 Elsevier Science B.V.

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1. Introduction

It is well known that the additivity rule with respect to the number of methylene groups holds very accurately for the partial molar volumes of n -alkane at infinite dilution. The chain length dependence of the partial molar volume at infinite dilution V_X^∞ of n -alkane in benzene at 298.15 K is shown in Fig. 1. In this figure, the straight line is obtained by the least squares method using the equation:

$$V_X^\infty = a + bn \quad (1)$$

for the data of pentane to decane. Here, n refers to the number of unit groups composing the chain molecules. The data point of ethane falls exactly on this line expressing the additivity rule for V_X^∞ of n -alkane. On the other hand, the data point of methane deviates slightly upward from this line. We can say from this figure that the additivity rule holds very accurately including very small alkanes except for methane.

However, the theoretical basis of this rule has not been made clear from the microscopic point of view. For macroscopic matter, the volume is the sum of its constituent part, and thus the additivity rule hold rigorously. On the other hand, the partial molar volume is the quantity determined through multi-body effects, and thus in principle the partial molar volume is not additive, especially for short chain length region. Thus, several contributions to the partial molar volume must cancel out each other in order for the additivity rule to hold. The elucidation of the mechanism affecting the additivity rule will give us an important sight to understand the liquid state in microscopic level.

We have calculated the partial molar volume of rigid chain molecules at infinite dilution by the RISM-PY integral equation [3] and shown that the hard-core model well explains the additivity rule of n -alkane and the conformation of solute molecule plays an important role for the additivity rule to hold, especially in short-chain length region. Since n -alkane is the flexible chain molecule, several conformers other than the extended form can exist in solutions to some extent. In order to investigate

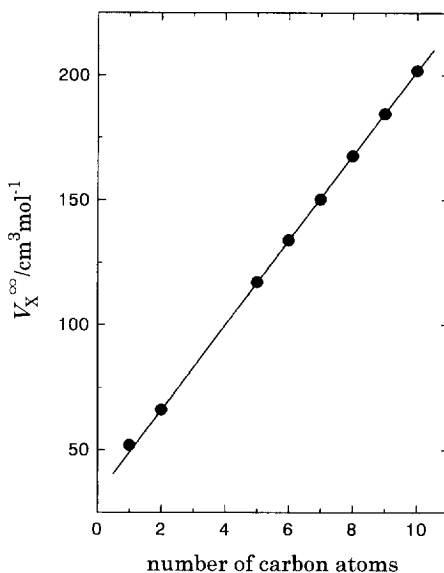


Fig. 1. Chain length dependence of the partial molar volume of n -alkane in infinitely dilute benzene solution at 298.15 K. The data of methane and ethane are found in Ref. [1]. The data of pentane to decane are found in Ref. [2].

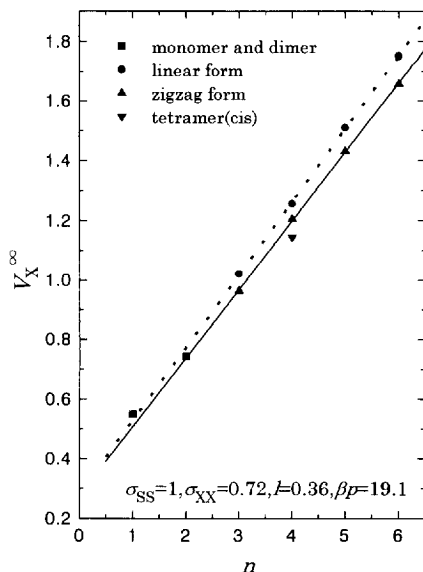


Fig. 2. Theoretical result of the partial molar volumes of model chain molecules.

the effect of the conformation and the flexibility of solute molecules, we have measured the partial molar volume of polycyclic aromatics.

In Section 1.1, we briefly described the theoretical results, and then the experimental results are discussed in the latter sections.

1.1. Partial molar volume of model fluids

Fig. 2 shows the chain length dependence of the partial molar volume of model fluids calculated using the RISM-PY integral equation whose details will be published elsewhere [3]. The molecular model used in this calculation is shown in Fig. 3. We call the solute molecules with the bond angle $\theta = \pi$ and $\theta = 2\pi/3$ the linear form and the zigzag form, respectively. Molecular parameters used in this calculation are $\sigma_{SS} = 1$, $\sigma_{XX} = 0.72$, $l = 0.36$, and the packing fraction of solvent $\eta_s = 0.5383$.

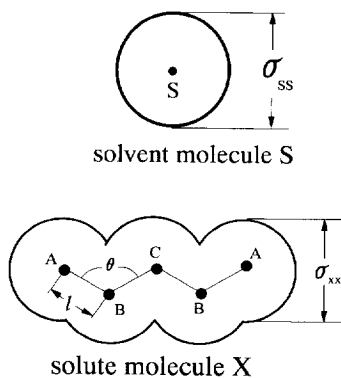


Fig. 3. Schematic representation of the model of molecules.

This value of η_s leads to $p/k_B T = 19.10$, and this in turn corresponds to the standard pressure of the liquid state for the system consisting of only one species with hard-sphere potential [4,5]. Here, p is the pressure, k_B the Boltzmann constant and T the absolute temperature. The solid line and dotted line in Fig. 2 are those obtained from the data point for trimer to hexamer with zigzag form and linear form, respectively.

The data point for dimer does not fall on the dotted line but falls exactly on the solid line. The value of monomer is somewhat larger than that expected from the additivity rule for zigzag form. Thus, it can be said that the calculated result of the set of monomer, dimer and trimer to hexamer with zigzag form well reproduces the chain length dependence of the partial molar volume of n -alkane described above. This result is consistent with the fact that the bond angle between methylene groups of n -alkane is nearly equal to $2\pi/3$. This suggests that the effect of flexibility of the chain of n -alkane molecules is small, while the effect of the conformation of solute molecules is significant. Recently, we have shown that the difference of the partial molar volumes between cis and trans isomers is described by the difference in the packing of molecules arising from the difference in shape of the hard core [5]. The partial molar volume of the cis forms of tetramer is also shown in Fig. 2. The difference of the partial molar volumes between cis and zigzag form of tetramer clearly shows the importance of the conformation of chain molecules in order for the additivity rule to hold.

2. Experimental

2.1. Materials

Benzene (Wako Pure Chemicals, Special grade reagent) was fractionary distilled with 1.2 m column. Naphthalene, anthracene (Wako Pure Chemicals Special grade reagent), phenanthrene (Tokyo Kasei TCI-UP), triphenylene (Tokyo Kasei TCI-GR), diphenyl (Tokyo Kasei TCI-GR), *o*-, *m*- and *p*-terphenyl (Tokyo Kasei TCI-EP), 1,3,5-triphenyl benzene (Tokyo Kasei TCI-GR), *p*-di-

Table 1
Partial molar volumes ($\text{cm}^3 \cdot \text{mol}^{-1}$) of polycyclic aromatics in infinitely dilute solutions at 298.15 K

Solutes	Solvents		
	Benzene	Chloroform	<i>p</i> -dioxane
Benzene	89.4 ^a	89.9	89.4
Naphthalene	124.0	122.7	124.6
Anthracene	161.7	157.6	159.9
Phenanthrene	158.0	155.2	158.7
Chrysene	ns	189.3	ns
Triphenylene	188.6	185.0	191.2
Diphenyl	149.72	148.7	150.6
<i>o</i> -Terphenyl	212.0	210.4	213.0
<i>m</i> -Terphenyl	209.2	208.4	210.3
<i>p</i> -Terphenyl	208.7	207.3	208.0
1,3,5-Triphenyl benzene	270.0	267.6	273.0

ns: not soluble.

^aThe molar volume of benzene.

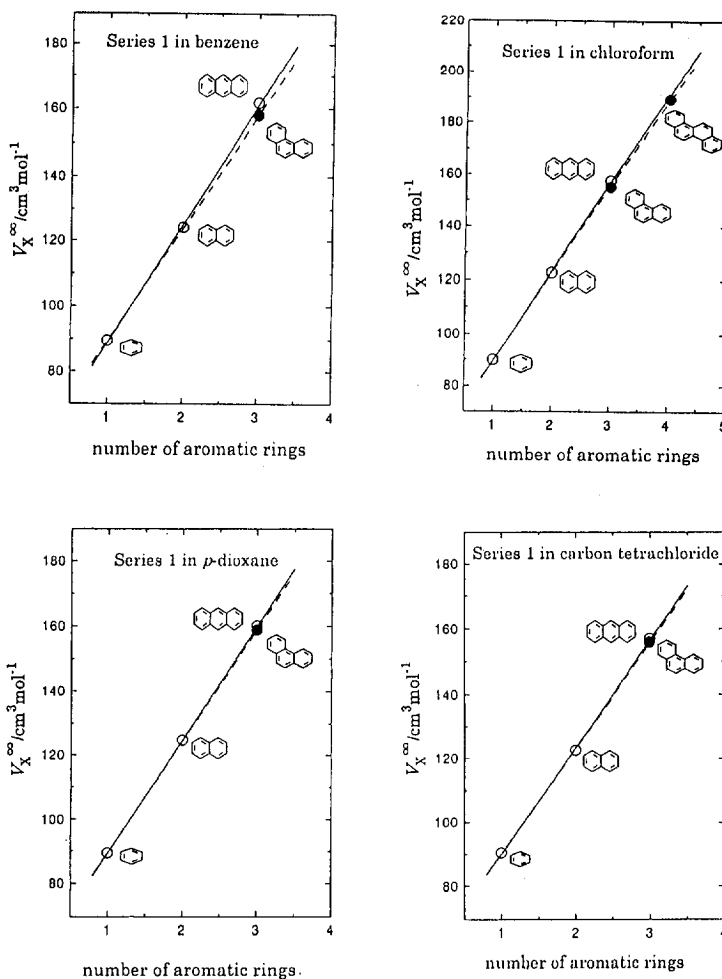


Fig. 4. Chain length dependence of the partial molar volumes of series 1 at 298.15 K. The experimental data in carbon tetrachloride are those of Shahidi et al. [6]. The solid line is obtained from the set of the data of benzene, naphthalene and anthracene. The broken line is obtained from the set of the data of benzene, naphthalene and phenanthrene (and chrysene for chloroform solution).

oxane (Wako Pure Chemicals Special grade reagent infinity pure, 99.8%) and chloroform (Wako Pure Chemicals Special grade reagent infinity pure, 99.9%) were used without further purification. The densities of benzene, chloroform and *p*-dioxane at 298.15 K are 0.87342 g/cm^3 , 1.47022 g/cm^3 and 1.02801 g/cm^3 , respectively.

2.2. Density measurement and evaluation of partial molar volumes

The digital high precision density meter DMA602 manufactured by Anton Paar was used. Solution density was measured at 298.15 K with precision of more than 0.001 K. As usual, the values of V_X^∞ were evaluated through the apparent molar volumes determined at three to four different concentrations.

3. Results and discussion

3.1. Additivity of the partial molar volume

Experimental results obtained are listed in Table 1. In order to ascertain the additivity of the partial molar volume, solute molecules are classified into two series. The series 1 is benzene, naphthalene, anthracene, phenanthrene and chrysene. The series 2 is benzene, diphenyl and *o*-, *m*- and *p*-terphenyl.

The chain length dependencies of series 1 are shown in Fig. 4. The data in carbon tetrachloride shown in this figure are those of Shahidi et al. [6]. In this figure, the solid line is obtained from the set of data of benzene, naphthalene and anthracene, and the broken line is obtained from the set of data of benzene, naphthalene, phenanthrene (and chrysene in chloroform). The coefficients *a* and *b* of Eq. (1) are listed in Table 2 together with the correlation coefficient *r*. In benzene solution, the linearity of the set of data of benzene, naphthalene and phenanthrene is clearly better than that of the set of data of benzene, naphthalene and anthracene. The similar tendency is found for solutions in carbon tetrachloride and chloroform. In *p*-dioxane, the linearities of both sets do not differ significantly. These results are confirmed by the correlation coefficients listed in Table 2.

The chain length dependencies of series 2 are shown in Fig. 5. In this figure, the solid line is obtained from the set of data for benzene, diphenyl and *p*-terphenyl. Because the difference of the partial molar volumes between *m*- and *p*-terphenyl is small, the linearity of the set of benzene, diphenyl and *p*-terphenyl and that of benzene, diphenyl and *m*-terphenyl are equal. On the other hand, the value of V_X^∞ of *o*-terphenyl clearly deviates upward from the solid line.

It is concluded that the additivity rule holds including monomer for both series 1 and 2. This behavior is different from the case of *n*-alkane shown in Fig. 1 and the theoretical result of model fluids shown in Fig. 2. The molecular parameters used in the calculation shown in Fig. 2 are suitable for *n*-alkane in benzene because the diameter of monomer is considerably smaller than that of solvent

Table 2

Solvent effect on the coefficients of Eq. (1). In the series 1 of each solvent, the values of the upper row are those obtained from the data of benzene, naphthalene and anthracene, and the values of the lower row are those of benzene, naphthalene, phenanthrene and chrysene. The values of series 1 in CCl₄ are calculated from the data in Ref. [6]. The values of *n*-alkane in C₆H₆ and CCl₄ are calculated from the data of pentane to decane in Refs. [2,7], respectively

	Solvent	<i>a</i>	<i>b</i>	<i>r</i>
series 1	C ₆ H ₆	52.73	36.15	0.9997
		55.20	34.30	1.0000
	CHCl ₃	55.70	33.85	0.9998
		56.60	33.07	0.9999
	<i>p</i> -C ₄ H ₈ O ₂	54.13	35.25	1.0000
		54.93	34.65	1.0000
series 2	CCl ₄	56.97	33.15	0.9998
		57.63	32.65	0.9999
	C ₆ H ₆	29.97	59.65	1.0000
	CHCl ₃	31.23	58.70	1.0000
	<i>p</i> -C ₄ H ₈ O ₂	30.73	59.30	0.9998
		30.73	59.30	0.9998
<i>n</i> -alkane	C ₆ H ₆	32.1	16.95	1.0000
	CCl ₄	33.4	16.53	1.0000

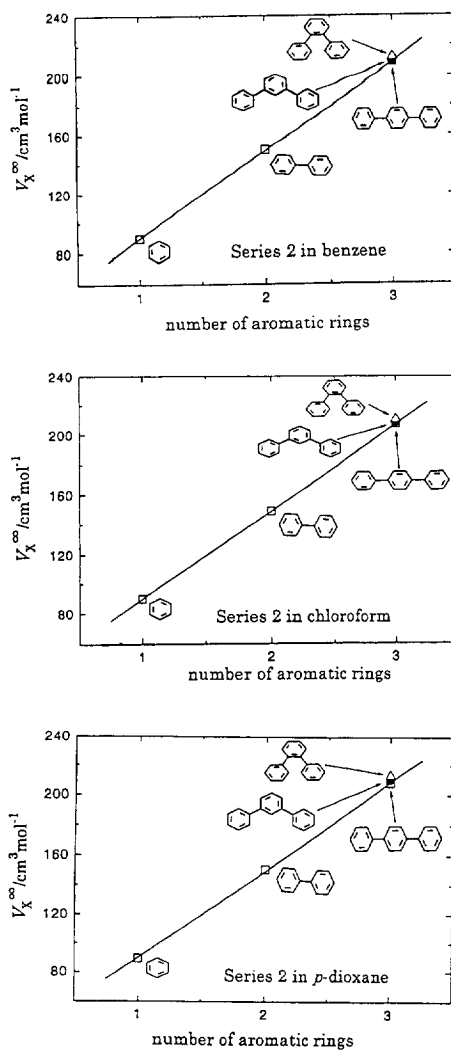


Fig. 5. Chain length dependence of the partial molar volumes of series 2 at 298.15 K. The solid line is obtained from the set of the data of benzene, diphenyl and *p*-terphenyl.

molecules. It may be possible that the additivity rule does not hold for methane because methane is considerably smaller than benzene. In order to investigate the effect of the size of monomer, we calculate the partial molar volume of model fluids whose molecular parameters are $(\sigma_{\text{SS}}, \sigma_{\text{XX}}, l) = (1, 1, 0.5)$ and $(1, 1, 0.9)$ which corresponds to series 1 and series 2, respectively, in benzene. The packing fraction of solvent is the same as in Fig. 2. The results are shown in Fig. 6. The solid line and dotted line for the series of $l = 0.5$ in Fig. 6 are those obtained from the data point for trimer to hexamer with zigzag form and linear form, respectively, which is the same as the case of Fig. 2, while the solid line for $l = 0.9$ is the one obtained from the data point for trimer to hexamer with linear form. In the case of $l = 0.9$, the chain length dependence of V_X^∞ for linear molecule is almost equal to that of zigzag molecule and the additivity rule holds including monomer. This result is in accordance

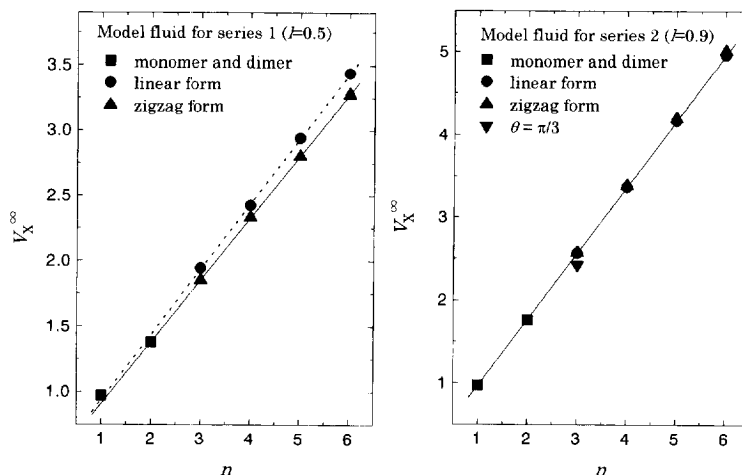


Fig. 6. Theoretical results of the partial molar volume of model fluids for series 1 and 2 in benzene.

with the behavior of series 2. On the other hand, the chain length dependence of V_X^∞ at $l = 0.5$, is qualitatively the same as that shown in Fig. 2, and the additivity rule holds except for monomer. This behavior does not agree with that of series 1. These results show the following fact as (1) the difference of the behavior of the monomer of polycyclic aromatics with n -alkane is not the size effect of monomer and (2) irrespective of the cause of the difference of the behavior of monomer, with increasing the bond length l the difference of the values of V_X^∞ between linear form and zigzag form becomes small, and the value expected from the additivity rule approaches the value of monomer.

3.2. Effect of the conformation of solute

Though the data of tetramer and higher oligomers are unavailable except for chrysene in chloroform, it seems that the linearity for the set of the data of monomer, dimer and zigzag conformers is better than that of monomer, dimer and linear conformers for series 1.

As shown in Table 1, the partial molar volume of anthracene is always larger than that of phenanthrene in all solvents studied. $\{V_{X,\text{anthracene}} - V_{X,\text{phenanthrene}}\}/V_{X,\text{anthracene}} = 0.023, 0.015, 0.008$ and 0.006 in benzene, in chloroform, in p -dioxane and in carbon tetrachloride [6], respectively. These values are comparable with the value of $\{V_{X,\text{linear}} - V_{X,\text{zigzag}}\}/V_{X,\text{linear}} = 0.047$ of our model fluids with the parameter set $(\sigma_{SS}, \sigma_{XX}, l) = (1, 1, 0.5)$. This conformation dependence agrees with our finding [5] that the partial molar volumes of trans decalin in several solvents are always larger than those of cis decalin and this behavior is well explained by the RISM-PY theory with model fluid system similar to the one used in this work. For many compounds having conformational isomers, the partial molar volume becomes larger as the molecule takes more stretched form.

On the other hand, among the partial molar volumes of three isomers of terphenyl in Table 1, the value of the partial molar volume becomes smaller as the molecule takes more stretched form. This behavior is quite opposite to many other compounds as described above. Interestingly, the values of V_X^∞ of trimer at $\theta = 2\pi/3$ in our theoretical result is slightly larger than that of $\theta = \pi$. However, the value of V_X^∞ at $\theta = \pi/3$ is smaller than that of $\theta = \pi$ and $\theta = 2\pi/3$, which disagrees with the case

of *o*-terphenyl. Kato et al. recently showed from the measurement of infrared spectra under high pressure that the dihedral angles of diphenyl [8] and *p*-terphenyl [9] in carbon disulfide decrease with increasing the pressure. This means that the partial molar volume of diphenyl and *p*-terphenyl becomes larger as the dihedral angle increases. Thus, the major cause of the peculiar behavior of V_X^∞ of terphenyls is probably the increase of the dihedral angle between two aromatic rings arising from the increase of the steric hindrance between two aromatic rings with decreasing bond angle θ . Enlargement of V_X^∞ due to the increase of dihedral angle along with the decrease of bond angle will exceed the decrease of V_X^∞ arising directly from the decrease of bond angle.

4. Conclusion

The chain length dependence of V_X^∞ for polycyclic aromatics in the small chain length region is different from that of *n*-alkane. In the case of *n*-alkane, the additivity rule holds except for methane, which is well reproduced by our theory for model molecules with the zigzag form. On the other hand, in the case of polycyclic aromatics, the additivity rule holds for solute molecules with the zigzag form including monomer. Our theoretical results suggest that this difference of behavior cannot be referred the size effect of monomer.

The conformational change of V_X^∞ for isomers of terphenyl is quite opposite to many other compounds. This peculiar behavior is referred to the increase of the dihedral angle between two aromatic rings along with the decrease of the bond angle.

In order to explain these behaviors, the partial molar volume data for solute having as long chain as possible and in various solvents are necessary for comparing these data with the results of the integral equation theory using the more refined molecular model.

5. List of symbols

V_X	partial molar volume of solute at infinite dilution
σ_{SS}	the hard-sphere diameter of solvent molecule
σ_{XX}	the hard-sphere diameter of solute molecule
θ	bond angle of model solute molecules

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