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# Semiempirical Relations in Molecular Liquids. II. Estimation of Thermal Expansivity

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A simple method for the estimation of thermal expansivity of the molecular liquid is proposed. Thermal expansivity $\alpha$ can be calculated by

$$\alpha = T^{-1}\phi(y)/y\phi'(y),$$

where $\phi(y)=p_h/\rho kT, y=\pi\rho a^3/6$, $p_h$ is the pressure of a hard sphere fluid, $a$ the effective hard core diameter of the molecule, $\rho$ the number density, and $k$, $T$ have their usual meanings. For the molecular liquids consisting of compact molecules, the equation gives a fairly accurate estimation of $\alpha$, which is practically applicable to the estimation of the density of the liquids at 1 atm at desired temperature.

If the effective hard core diameter of the molecule and the density of the liquid are known, then the scaled particle theory (SPT) allows one to calculate surface tension, compressibility, *etc.* of the molecular liquids.[1] From knowledge of the density at room temperature and the approximate value of melting temperature, which are both easily measurable, hard core diameter $a$ at desired temperature can be estimated by the method given in the preceding paper.[2]

If the value of thermal expansivity $\alpha$ calculated by the SPT were accurate, then the density at desired temperature could be estimated from the melting point and the density at room temperature. However, $\alpha$ estimated by the SPT is not sufficiently accurate for practical use.

The purpose of the present paper is to propose a method for the fairly accurate estimation of $\alpha$ from the effective hard core diameter of molecule and density. This method enables one to calculate the density at desired temperature at 1 atm from the melting point and the density at room temperature.

## Theory

It is an oversimplified assumption that the volume change at higher densities is mainly due to the repacking of molecular hard cores.[1] Hence the effect of intermolecular attractive forces on the equation of state must be taken into account. The simplest method is to adopt the so-called augmented van der Waals (AVdW) equation of state,[3]

$$p = p_h - \varepsilon\rho^2, \tag{1}$$

where $\rho$ is the number density, $p$ the pressure, $p_h$ the pressure of a hard sphere fluid with hard core diameter $a$, and $\varepsilon$ a constant. Since $p_h/\rho kT$ is the function of $y=\pi\rho a^3/6$ only, we put $p_h=\rho kT\phi(y)$. Thermal expansivity $\alpha$ is given by

$$(\alpha T)^{-1} = (\partial \ln T/\partial \ln V)_p. \tag{2}$$

From Eqs. (1) and (2), taking into account that $p\ll\varepsilon\rho^2$ at higher densities, we obtain

$$(\alpha T)^{-1} = -1 + y\phi'(y)/\phi(y). \tag{3}$$

If $\varepsilon=0$, *i.e.*, $dp=dp_h$, then[1]

$$(\alpha T)^{-1} = 1 + y\phi'(y)/\phi(y). \tag{4}$$

However, the value of $\alpha T$ predicted by Eq. (3) is too large and that by Eq. (4) is too small.

According to the computer experiment by Alder and Hecht,[4] $\varepsilon$ strongly depends on $y$ at higher densities. Hence it is suggested that the crudest modification of the AVdW equation of state is to assume $\varepsilon$ to be proportional to $y^{-1}$ at higher densities ($y\gtrsim 0.4$). After modification of Eq. (1), we obtain

$$(\alpha T)^{-1} = y\phi'(y)/\phi(y). \tag{5}$$

In deriving Eqs. (3)—(5), the contribution of $da/dT$ is not taken into account, since all the quantities are calculated for the model liquid consisting of hard spheres exerting attractive forces. The diameter of the hard sphere is so chosen after all the calculations are completed to describe the molecular liquid at temperature $T$. Note that $\alpha T$ does not depend on the details of the intermolecular attractive forces. In the following, we adopt the Carnahan-Stahling equation of state[5] for $\phi(y)$.

## Comparison with Observed Data

The observed values of $\alpha T$ at 298 K for organic liquids of nearly spherical molecules and the calculated values of $\alpha T$ given by Eqs. (3)—(5) are plotted *vs.* $y$ which is obtained by means of

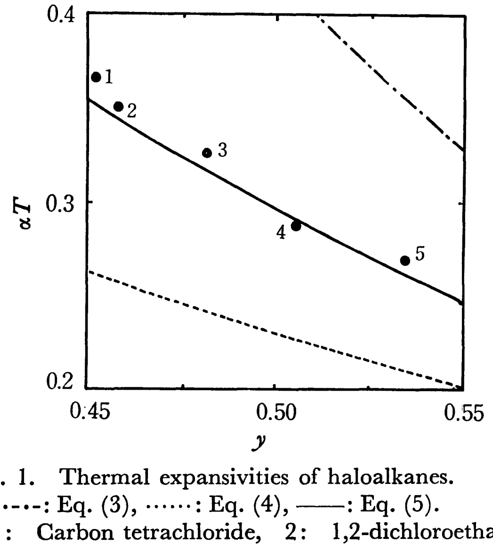

Fig. 1. Thermal expansivities of haloalkanes.
-·-·-: Eq. (3), ······: Eq. (4), ——: Eq. (5).
1: Carbon tetrachloride, 2: 1,2-dichloroethane, 3: bromotrichloromethane, 4: 1,2-dibromoethane, 5: 1,3-dibromopropane.

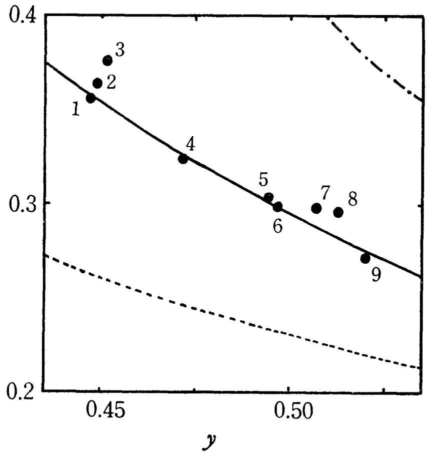

Fig. 2. Themal expansivities of benzene and mono-substituted benzenes.
-·-·-: Eq. (3), ······: Eq. (4), ——: Eq. (5).
1: Fluorobenzene, 2: benzene, 3: (trifluoromethyl)-benzene, 4: toluene, 5: ethylbenzene, 6: chlorobenzene, 7: cumene, 8: propylbenzene, 9: bromobenzene.

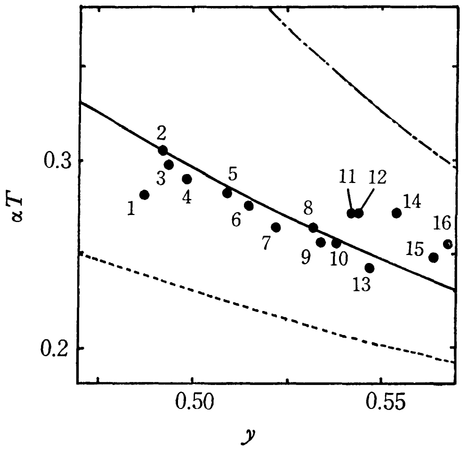

Fig. 3. Thermal expansivities of di- and tri-substituted benzenes.
-·-·-: Eq. (3), ······: Eq. (4), ——: Eq. (5).
1: *p*-Dichlorobenzene, 2: *p*-xylene, 3: *m*-xylene, 4: *o*-xylene, 5: 1,3,5-trimethylbenzene, 6: 1,2,4-trimethylbenzene, 7: 1,2,3-trimethylbenzene, 8: *m*-dichlorobenzene, 9: *o*-dichlorobenzene, 10: *o*-cresol, 11: *p*-ethylpropylbenzene, 12: *p*-*t*-butyltoluene, 13: 3,4-dichlorotoluene, 14: *p*-diisopropylbenzene, 15: *o*-ethylnitrobenzene, 16: *o*-diisopropylbenzene.

$$\sigma T^{-1}\rho^{-2/3} = 4.28\times 10^{-17}y^{1/3}(2+y)/(1-y)^2, \qquad (6)$$

where $\sigma$ is the surface tension in dyn/cm.[1,2] (Figs. 1—5). The observed data on thermal expansivity at 298 K are calculated by $(\rho_{293\,\mathrm{K}}-\rho_{303\,\mathrm{K}})/5(\rho_{293\,\mathrm{K}}+\rho_{303\,\mathrm{K}})$. The data on density and surface tension are obtained from Refs. 6—8. Surface tension scarcely depends on the details of the intermolecular attractive forces,[2] so that use of $y$ estimated from Eq. (6) is suitable. Figures 1—5 show that $\alpha T$ of organic liquids of nearly spherical molecules without strong dipole moments and strongly hydrogen-bonding abilities satisfy Eq. (5), but not Eqs. (3) and (4).

Figure 6 shows that organic liquids of long chain-like molecules deviate considerably from Eq. (5). The deviation is not surprising since the SPT is so constructed as to treat liquids of spherical molecules.

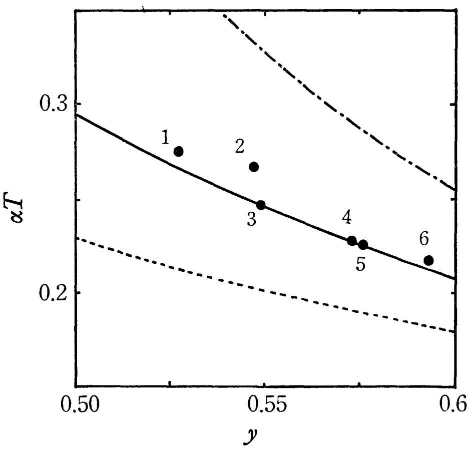

Fig. 4. Thermal expansivities of naphthalenes *etc.*
-·-·-: Eq. (3), ······: Eq. (4), ——: Eq. (5).
1: *trans*-Decalin, 2: *cis*-decalin, 3: tetralin, 4: 5-methyl-1,2,3,4-tetrahydronaphthalene, 5: 1-methylnaphthalene, 6: 2-butylnaphthalene.

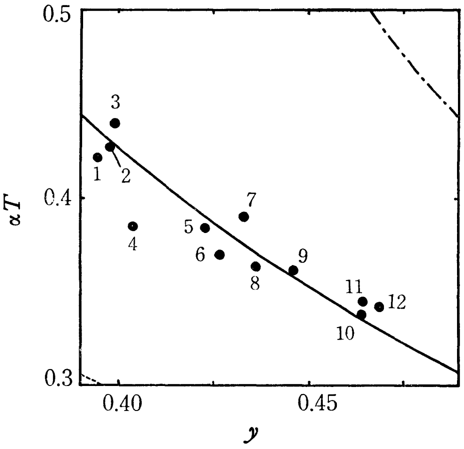

Fig. 5. Thermal expansivities of aliphatic compounds.
-·-·-: Eq. (3), ······: Eq. (4), ——: Eq. (5).
1: 2,3-Dimethylbutane, 2: 2-methylpentane, 3: 2-pentyne, 4: propionitrile, 5: ethyl methyl sulfide, 6: 2,2,3-trimethylbutane, 7: 2,3-dimethyl-2-butene, 8: 3,3-dimethylpentane, 9: 2,2,4-trimethylpentane, 10: butyronitrile, 11: 2-methylhexane, 12: 3-ethyl-2-methylpentane.

## Applications

*Estimation of* $\rho$–$T$ *Relation at 1 atm.* As an application of the results of the preceding and the present papers, we show how to estimate $\rho$ at $T$ from the melting point and the density $\rho_0$ at temperature $T_0$. The effective hard core diameter $a$ at melting point can be calculated from the melting point and the molecular structure. The effective hard core diameter $a_0$ at $T_0$ can be obtained by Eq. (6) from $\rho_0$ and parachor. Then we can calculate $\alpha$ at $T_0$ by means of Eq. (5). With the value of $\alpha$ obtained, we can estimate the density at $T_0+\Delta T$ by $\rho=(1-\alpha\Delta T)\rho_0$. The procedure is repeated until the desired temperature is reached. Some examples are given in Tables 1—4, where $\Delta T$ is

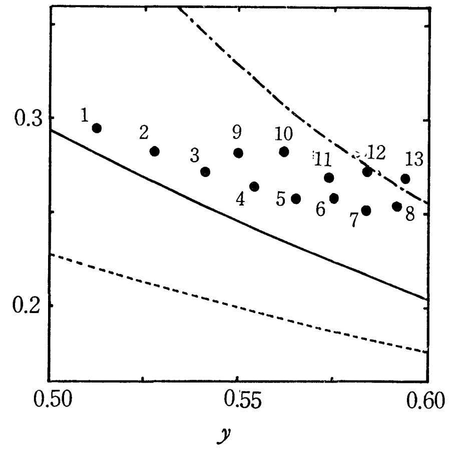

Fig. 6. Thermal expansivities of normal alkanes and their phenyl derivatives.
-----: Eq. (3), ······: Eq. (4), ——: Eq. (5).
1: Propylbenzene, 2: butylbenzene, 3: pentylbenzene, 4: hexylbenzene, 5: heptylbenzene, 6: octylbenzene, 7: nonylbenzene, 8: decylbenzene, 9: dodecane, 10: tridecane, 11: tetradecane, 12: pentadecane, 13: hexadecane.

10 K. It can be concluded that the method mentioned above provides a fairly accurate and practical procedure for the estimation of $\rho - T$ relation at 1 atm.

Table 1. Estimation of the specific volume of chloroform

The density at 293 K is 1.4894 g/cm$^3$,[13] which is assumed to be known. From this data and the melting point 210 K, $da/dT$ becomes $4.14 \times 10^{-3}$ Å/K. The specific volume at supercooled state is predicted accurately.

| $T$(K) | Specific volume (cm$^3$/g) | |
|---|---|---|
| | Obsd[13] | Calcd |
| 283 | 0.6634 | 0.6630 |
| 273 | 0.6554 | 0.6546 |
| 263 | 0.6473 | 0.6465 |
| 253 | 0.6393 | 0.6388 |
| 243 | 0.6321 | 0.6313 |
| 233 | 0.6243 | 0.6241 |
| 223 | 0.6172 | 0.6172 |
| 213 | 0.6106 | 0.6106 |
| 203 | 0.6039 | 0.6042 |

Table 2. Estimation of the specific volume of chlorobenzene

The density at 293 K is 1.055 g/cm$^3$,[13] which is assumed to be known. From this data and the melting point 228 K, $da/dT$ becomes $2.45 \times 10^{-3}$Å/K.

| $T$(K) | Specific volume (cm$^3$/g) | |
|---|---|---|
| | Obsd[13] | Calcd |
| 283 | 0.8956 | 0.8957 |
| 273 | 0.8868 | 0.8870 |
| 263 | 0.8789 | 0.8784 |
| 253 | 0.8696 | 0.8700 |
| 243 | 0.8621 | 0.8616 |
| 233 | 0.8532 | 0.8534 |
| 228 | 0.8494 | 0.8494 |

Table 3. Estimation of the specific volume of bromobenzene

The density at 293 K is 1.4954 g/cm$^3$,[13] which is assumed to be known. From this data and the melting point 243 K, $da/dT$ becomes $2.22 \times 10^{-3}$/K.

| $T$(K) | Specific volume (cm$^3$/g) | |
|---|---|---|
| | Obsd[13] | Calcd |
| 323 | 0.6877 | 0.6876 |
| 313 | 0.6813 | 0.6812 |
| 303 | 0.6746 | 0.6749 |
| 283 | 0.6632 | 0.6626 |
| 273 | 0.6566 | 0.6566 |
| 263 | 0.6507 | 0.6507 |
| 253 | 0.6452 | 0.6449 |
| 243 | 0.6397 | 0.6392 |
| 234.5 | 0.6353 | 0.6343 |

Table 4. Estimation of the specific volume of nitrobenzene

The density at 293 K is 1.2019 g/cm$^3$,[13] which is assumed to be kmnown. From this data and the melting point 278.8 K, $da/dT$ becomes $4.07 \times 10^{-3}$Å/K.

| $T$(K) | Specific volume (cm$^3$/g) | |
|---|---|---|
| | Obsd[13] | Calcd |
| 283 | 0.8258 | 0.8251 |
| 303 | 0.8380 | 0.8389 |
| 313 | 0.8452 | 0.8457 |
| 323 | 0.8517 | 0.8525 |

*Liquid Argon at Triple Point.* We have proposed the modification of the AVdW equation of state. This equation of state gives good estimation of $\alpha$ and isothermal compressibility $\beta$ of liquid argon at triple point. Longuet-Higgins and Widom[3] and Guggenheim[9] estimated $\alpha$ and $\beta$ of liquid argon at triple point using the AVdW equation of state. The values obtained by Longuet-Higgins and Widom are $\alpha T = 0.50$ and $\rho k T \beta = 0.058$. Guggenheim estimated $y$ at triple point to be 0.427 from the data of internal pressure, and obtained $\alpha T = 0.57$ and $\rho k T \beta = 0.0663$. The observed values are $\alpha T = 0.37$ and $\rho k T \beta = 0.0495$.[3]

Using the modified AVdW equation of state,

$$\frac{p}{\rho kT} = \frac{1+y+y^2-y^3}{(1-y)^3} - \varepsilon' y, \tag{7}$$

where $\varepsilon'$ is a constant, and the data of internal pressure used by Guggenheim, we obtain $y = 0.422$ at triple point. From this value of $y$ we obtain $\alpha T = 0.39$ and $\rho k T \beta = 0.050$. These values agree well with the observed data.

## Discussion

The effective hard core diameter can be calculated also from the data of isothermal compressibility.[1] The expression of isothermal compressibility in terms of $y$ has been derived from the following considerations.[1] At higher densities the isothermal compression can be regarded as a process of repacking hard spheres. Thus

$$dp = dp_h. \tag{8}$$

The isothermal compressibility can be approximately expressed by

$$\beta = \rho^{-1}(\partial\rho/\partial p_h)_T. \tag{9}$$

If we adopt the equation of state of hard sphere fluid obtained from the original SPT, then we have in cgs unit

$$\rho\beta T = 7.2\times10^{15}f(y), \tag{10}$$

where $$f(y) = (1-y)^4/(1+2y)^2. \tag{11}$$

If we adopt the Carnahan-Stahling equation of state, then Eq. (11) is replaced by

$$f_{SC}(y) = (1-y)^4/[(1+2y)^2+y^4-4y^3]. \tag{12}$$

Function $f_{SC}(y)$ is slightly larger than $f(y)$. Using the observed values for $\rho$, $\beta$, and $T$, we can calculate the effective hard core diameter $a_\beta$ of the molecule from Eq. (10).

Calculating $a_\beta$ from Eq. (10) and Eq. (11), and $a$ from Eq. (6), Mayer[10] has shown that $a_\beta$ and $a$ coincide with each other at room temperature. However, $da/dT$ is about twice as large as $da_\beta/dT$. This suggests that the temperature range in which $a_\beta$ and $a$ are nearly equal is not wide and that there is no universal relation between $\sigma$ and $\beta$. If there is a certain general relation between $\sigma$ and $\beta$ (as suggested by the SPT), the observed value of $\rho\beta T$ should be a one-valued function of $y$ obtained from Eq. (6). Some examples of $\rho\beta T$-$y$ relations are shown in Fig. 7 together with those calculated by using Eqs. (11) and (12). Figure 7 shows that, as expected, no universal relation exists between $\beta$ and $\sigma$. At higher densities Eq. (12) is more accurate than Eq. (11). This corresponds to the accuracy of the Carnahan-Stahling equation of state at higher densities.

Since $\sigma$ scarcely depends on the details of intermolecular forces, it can be concluded that $\beta$ depends on the details of intermolecular forces in comparison with $\sigma$. Thus the assumption (8) is concluded to be oversimplified.

In contrast to this $\rho\beta T$-$y$ relation, the temperature range in which Eq. (5) holds is not very narrow as is shown in Fig. 8.

The internal pressure calculated from the modified AVdW equation of state (7) is proportional not to $\rho^2$ but to $\rho$. This contradicts with the observation by Bianchi *et al.*[11] and also with an intuitive picture of the liquid state.[12] However, the modified AVdW equation of state predicts $\alpha$ fairly accurately and thus has a practical value. The original AVdW equation of state, which gives the internal pressure in proportion to $\rho^2$, gives poor results for $\alpha$ of molecular liquids and for the properties of liquid argon at triple point. As long as we use the van der Waals type equation of state, *i.e.*, $p=p_h-$(effect of intermolecular attractive forces), it is very difficult to work out the equation of state which predicts $\alpha$ accurately and at the same time gives the internal pressure in proportion to $\rho^2$. Thus there seems to be a limitation to the van der Waals type equation of state even at lower temperatures.

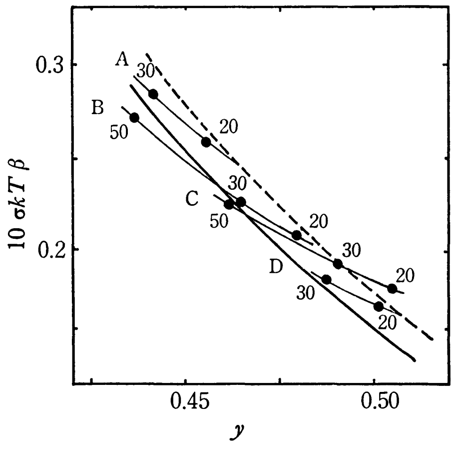

Fig. 7. Relation between compressibility and $y$. The numbers in the figure denote temperature in °C.
A: Benzene, B: toluene, C: chlorobenzene, D: *m*-xylene.
——: Eq. (11), ······: Eq. (12).

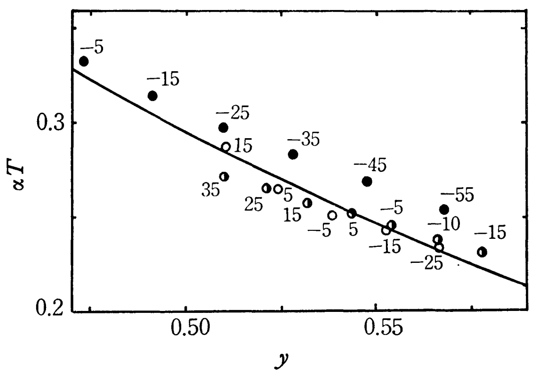

Fig. 8. Relation between thermal expansivity and $y$. The numbers in the figure denote temperature in °C. ●: Chloroform, ◑: bromobenzene, ○: chlorobenzene. ——: Eq. (5).

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