

## **Corresponding states correlations with potential between functional groups for thermodynamic properties of liquid n- and i-alkanes**

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### **Abstract**

For liquid n-alkanes  $C_1$  to  $n-C_{21}$  and i-alkanes i- $C_4$  to i- $C_{10}$  the interactions between the molecules are described with the use of potentials between the functional groups (inter-group potentials). The molar volume of liquid in saturation and the vapor pressure are correlated in the corresponding states method well and the surface tension is correlated satisfactorily with the use of the inter-group potential parameters and distance correction parameters. The correlations are better than those with the use of intermolecular potential parameters without the use of the inter-group potentials. The distance correction parameters can be fitted by functions of the location and the number of the groups in the molecule. The thermodynamic properties of the heavier liquid n-alkanes  $n-C_{22}$  to  $C_{30}$ ,  $C_{32}$  and  $C_{36}$ , which are not used for the parameters evaluation, can be predicted satisfactorily in the corresponding states method with the inter-group potential parameters and the distance correction parameter functions.

**Keywords:** corresponding states correlation, volume, vapor pressure, surface tension, liquid alkane, functional group

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## 1. Introduction

Liquid alkanes are of fundamental importance for chemical industries with their thermodynamic properties important to chemical process design. Although it is desirable to use the observed physical properties, the properties of all the alkanes and their mixtures for the various compositions and operated conditions are not available. The estimation or correlation equations of them are desired and the equations for the pure alkanes should be established as the first step.

Equation of state (EOS) is one of the useful methods for estimation or correlation of the thermodynamic properties. Cubic EOSs of the van der Waals type are often used due to their simplicity and accuracy. Many popular cubic EOSs are based on the PR EOS [1] and the SRK EOS [2,3]. Many modifications of them have been proposed to improve the accuracy for liquid density or vapor pressure. For the PR EOS, Stryjek and Vera [4,5] modified the function  $\alpha(t)$  and Xu and Sandler [6] introduced temperature dependency of the parameter  $b$ . The function  $\alpha(t)$  and the parameter  $b$  need the critical properties and the acentric factor  $\omega$ . For the SRK EOS, Peneloux et al. [7] introduced translating volume  $c$  in terms of the critical properties and the acentric factor into the EOS and Wang and Gmehling [8] modified the acentric factor dependence of  $\alpha(t)$ . The critical properties and the acentric factor or the shape parameter  $m$  that has a similar role to the acentric factor are all fluid specific. Although Wang and Gmehling and Carrier et al. [9] estimated the acentric factor or the shape parameter based on the group contribution concept, the critical properties or the normal boiling temperature are required.

The law of corresponding states is also one of simple and reliable methods for estimation and correlation of the thermodynamic properties. Teja and Sandler [10] modified the Lee-Kesler equation. They used two reference fluids and expanded a fluid

of interest around the first reference fluid with the difference of the acentric factors between the fluid of interest and the first reference fluid reduced by that between the two reference fluids. Although the PVT and the saturated density for LNG mixtures were estimated with the first perturbation term with good results, the properties of the fluid of interest should be between those of the two reference fluids or near one of the two reference fluids and it would be dangerous to make a long extrapolation.

Alkanes do not have many kinds of functional groups. The parameters of the potential between the functional groups, which we call inter-group potential in this paper, are not fluid specific. The law of corresponding states with the inter-group potentials can give a practical method for correlating and estimating the thermodynamic properties of the liquid alkanes including the isomers when the location and the number of the groups in the alkanes are taken into account. The aim of this paper is to obtain the corresponding states equations for the thermodynamic properties of the liquid alkanes including the isomers with the use of the inter-group potential parameters, which are not fluid specific.

In the present work, the intermolecular potential of an alkane of interest is expressed by the inter-group potential parameters and their distance correction parameters. The latter parameters depend on the location and the number of the groups in the molecule. The excess Helmholtz free energy of the alkane is expanded around that of a reference fluid, the intermolecular potential of which is expressed by the sum of a hard sphere potential and an attractive potential, with the difference between the core repulsive potentials. The hard sphere diameter is chosen such that the Helmholtz free energy of the alkane is equal to that of the reference. The corresponding states correlations of the thermodynamic properties, such as the molar volume, the vapor pressure and the surface tension, of the liquid alkanes are obtained with the use of the hard sphere diameter and

the potential depth of the reference fluid, which are evaluated by the inter-group potential parameters and the distance correction parameters. The results are found to be better than those with the use of the intermolecular potential parameters without the inter-group potential parameters. The distance correction parameters can be expressed as functions of the location and the number of the functional groups in a molecule. The corresponding states correlations are applied to heavier n-alkanes in n-C<sub>22</sub> to n-C<sub>36</sub>, which are not used for the evaluation of the inter-group potential parameters and the distance correction parameters.

## 2. Characteristic length and energy

### 2.1. Intermolecular potential parameters and inter-group potential parameters

We consider a model that the intermolecular potential between molecules 1 and 2 of a fluid  $v(r)$ , which is expressed by the sum of potentials between the functional groups  $l$  and  $m$ , that is, the inter-group potentials  $\phi^{lm}$ .

$$v(r) = \sum_l \sum_m \phi^{lm}(r^{lm}) \quad (1)$$

The sum is taken over all the functional groups  $l$  and  $m$  in molecules 1 and 2, respectively. Both are to be given by Lennard-Jones 12-6 potentials.

$$v(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (2)$$

$$\phi^{lm}(r) = 4\varepsilon^{lm} \left[ \left( \frac{\sigma^{lm}}{r^{lm}} \right)^{12} - \left( \frac{\sigma^{lm}}{r^{lm}} \right)^6 \right] \quad (3)$$

where  $\varepsilon$  and  $\sigma$  are the intermolecular potential parameters and  $r$  is the distance between molecules 1 and 2.  $\varepsilon^{lm}$  and  $\sigma^{lm}$  are the inter-group potential parameters and  $r^{lm}$  is the distance between the functional groups  $l$  and  $m$ .

When alkane molecules are set in a distance averaged for their configurations  $d$ , which is called a characteristic length, the intermolecular potential,  $v(d)$ , is written by the inter-group potentials at the distance between the functional groups  $l$  and  $m$ ,  $d^{lm}$ .

$$v(d) = \sum_l \sum_m \phi^{lm}(d^{lm}) \quad (4)$$

It is assumed that the repulsive part and the attractive part of the intermolecular potential are to be equal to those of the inter-group potentials, respectively.

$$4\varepsilon \left( \frac{\sigma}{d} \right)^{12} = \sum_l \sum_m 4\varepsilon^{lm} \left( \frac{\sigma^{lm}}{d^{lm}} \right)^{12} \quad (5)$$

$$4\varepsilon \left( \frac{\sigma}{d} \right)^6 = \sum_l \sum_m 4\varepsilon^{lm} \left( \frac{\sigma^{lm}}{d^{lm}} \right)^6 \quad (6)$$

We set that  $d^{lm} = d + \Delta^{lm}$ , where  $\Delta^{lm}$  is the correction for the distance between groups  $l$  and  $m$ , which depends on the locations and the numbers of the functional groups in the molecule. The characteristic length  $d$  and the distances between the groups  $d^{lm}$ s for propane are shown in Fig. 1 as an example. There are three kinds of inter-group distances,  $d^{CH3-CH3}$ ,  $d^{CH3-CH2}$  and  $d^{CH2-CH2}$ , which are averaged distances between CH<sub>3</sub>s, between CH<sub>3</sub> and CH<sub>2</sub> and between CH<sub>2</sub>s. Dashed line is the characteristic length  $d$  and dot line, dashed-dot line and dashed-two dot line are the inter-group distances  $d^{CH3-CH3}$ ,  $d^{CH3-CH2}$  and  $d^{CH2-CH2}$ , respectively, in the figure.

After substitution of  $d^{lm} = d + \Delta^{lm}$  into Eqs. (5) and (6) and some algebra  $\varepsilon$  and  $\sigma$  can be written as Eqs. (7) and (8), respectively.

$$\varepsilon = \frac{\left[ \sum_l \sum_m \varepsilon^{lm} \left( \frac{\sigma^{lm}}{d + \Delta^{lm}} \right)^6 \right]^2}{\sum_l \sum_m \varepsilon^{lm} \left( \frac{\sigma^{lm}}{d + \Delta^{lm}} \right)^{12}} \quad (7)$$

$$\sigma = \left[ \frac{\sum_l \sum_m \varepsilon^{lm} \left( \frac{\sigma^{lm}}{d + \Delta^{lm}} \right)^{12}}{\sum_l \sum_m \varepsilon^{lm} \left( \frac{\sigma^{lm}}{d + \Delta^{lm}} \right)^6} \right]^{1/6} \times d \quad (8)$$

Eqs. (7) and (8) show that  $\varepsilon$  and  $\sigma$  depend on  $\varepsilon^{lm}$ ,  $\sigma^{lm}$ ,  $d$  and  $\Delta^{lm}$ .  $d$  is a weak function of temperature as shown later, thus  $\varepsilon$  and  $\sigma$  weakly depend on temperature.

## 2.2. Characteristic length $d$

The intermolecular potential  $v(r)$  of the fluid of interest is separated into a repulsive part  $v^0(r)$  and an attractive part  $w(r)$  with WCA(Weeks-Chandler-Andersen) method [11].

$$v(r) = v^0(r) + w(r) \quad (9)$$

$$\begin{aligned} v^0(r) &= v(r) + \varepsilon, & r \leq r_m = 2^{1/6} \sigma \\ &= 0, & r > r_m \end{aligned} \quad (10)$$

$$\begin{aligned} w(r) &= -\varepsilon, & r \leq r_m \\ &= v(r), & r > r_m \end{aligned} \quad (11)$$

The intermolecular potential for a reference fluid  $v^{ref}(r)$  is made up of a hard sphere potential  $v^{hs}(r)$  and the attractive potential  $w(r)$ .

$$v^{ref}(r) = v^{hs}(r) + w(r) \quad (12)$$

$$\begin{aligned} v^{hs}(r) &= \infty, & r \leq d \\ &= 0, & r > d \end{aligned} \quad (13)$$

The hard sphere diameter of the reference  $d$ , which is the characteristic length, is evaluated from the perturbation expansion of the excess Helmholtz free energy in the method of Harada et al. [12]. When  $d$  is chosen such that Eq. (14) holds, the excess free energy of the fluid of interest is equal to that of the reference, Eq. (15) (See Appendix

A).

$$d^3 / 3 = \int_d^\infty [\exp(\beta v^0) - 1] r^2 dr \quad (14)$$

$$\hat{A}^{ex} = \beta A^{ex} = \beta A^{ex,ref} = \hat{A}^{ex,ref} \quad (15)$$

Eq. (15) shows a simple thermodynamic equation expressing the law of corresponding states.

The  $d$  value is numerically calculated from Eq. (14) and the resultant values are fitted by the function (16).

$$d / \sigma = 0.9573 + 5.020 \times 10^{-2} \ln (\varepsilon / kT) - 5.157 \times 10^{-3} (\varepsilon / kT) \quad (16)$$

Strictly speaking, the  $d$  value depends on the density because the radial distribution function depends on the density. This minor density dependency of  $d$  is not included in Eq. (16).

### 3. Corresponding states equations of thermodynamic properties

Eq. (15) shows that the fluid of interest and the reference are in the corresponding states and the thermodynamic properties derived from the Helmholtz free energy, that is, molar volume, vapor pressure and surface tension, along the saturation curve can be related to the following universal functions if the density dependency of the  $d$  value is neglected.

$$\hat{V} = \frac{V}{N_A d^3} = \hat{V}^{ref}(\hat{T}) \quad (17)$$

$$\hat{p} = \frac{p d^3}{\varepsilon} = \hat{p}^{ref}(\hat{T}) \quad (18)$$

$$\hat{\gamma} = \frac{\gamma d^2}{\varepsilon} = \hat{\gamma}^{ref}(\hat{T}) \quad (19)$$

where

$$\hat{T} = \frac{kT}{\varepsilon} \quad (20)$$

#### 4. Evaluation of inter-group potential parameters and separation distance correction parameters

The potential parameters needed for the correlations are the following six parameters,  $\varepsilon^{CH_3-CH_3}$ ,  $\varepsilon^{CH_3-CH_2}$  ( $= \varepsilon^{CH_3-CH}$ ),  $\varepsilon^{CH_2-CH_2}$  ( $= \varepsilon^{CH_2-CH} = \varepsilon^{CH-CH}$ ),  $\sigma^{CH_3-CH_3}$ ,  $\sigma^{CH_3-CH_2}$  ( $= \sigma^{CH_3-CH}$ ) and  $\sigma^{CH_2-CH_2}$  ( $= \sigma^{CH_2-CH} = \sigma^{CH-CH}$ ). The values of the parameters are not specific to each pure compound but are common for n-alkanes and common for i-alkanes.

The distance correction parameters  $\Delta^{lm}$ s are needed to each pure compound. N-alkanes and 2-methylalkanes need the three parameters  $\Delta^{CH_3(N)-CH_3(N)}$ ,  $\Delta^{CH_3(N)-CH_2(n)}$  and  $\Delta^{CH_2(n)-CH_2(n)}$ . 3- or more than 3-methylalkanes need the six parameters  $\Delta^{CH_3(N)-CH_3(N)}$ ,  $\Delta^{CH_3(N)-CH_3(N')}$ ,  $\Delta^{CH_3(N')-CH_3(N')}$ ,  $\Delta^{CH_3(N)-CH_2(n)}$  ( $= \Delta^{CH_3(N)-CH(n)}$ ),  $\Delta^{CH_3(N')-CH_2(n)}$  ( $= \Delta^{CH_3(N')-CH(n)}$ ) and  $\Delta^{CH_2(n)-CH_2(n)}$  ( $= \Delta^{CH_2(n)-CH(n)} = \Delta^{CH(n)-CH(n)}$ ) because  $N \neq N'$ . Here  $N$  and  $N'$  mean the location of the group  $CH_3$  and  $n$  means the number of the groups  $CH_2$  and  $CH$  in a molecule. It is assumed for simplicity that the distance correction for the group  $CH_3$  just depends on the location  $N$  and the groups that are not at the end of the molecule,  $CH_2$  and  $CH$ , are not distinguished from each other. From the latter assumption the parameters between the functional groups  $CH_3-CH_2$  and  $CH_3-CH$ , and  $CH_2-CH_2$ ,  $CH_2-CH$  and  $CH-CH$  are equal to each other as shown above and the distance correction parameters  $\Delta^{CH_2(n)-CH_2(n)} = \Delta^{CH_2(n)-CH(n)} = \Delta^{CH(n)-CH(n)}$  just depend on the number of the groups  $n$ .  $N$  is defined as the location of the carbon atom counted from the center in the main chain of the molecule.  $N$  is integer when the center is at a carbon atom and  $N$  has fraction 0.5 when the center is at a bond between two carbon atoms. The use of  $\Delta^{lm}$ s can distinguish among the isomers and correlate the thermodynamic properties in the



corresponding states as shown later.

For example,  $N = 1$  and  $n = 1$  and  $\Delta^{CH_3(1)-CH_3(1)}$ ,  $\Delta^{CH_3(1)-CH_2(1)}$  and  $\Delta^{CH_2(1)-CH_2(1)}$  are needed for propane and  $N = 1.5$  and  $n = 2$  and  $\Delta^{CH_3(1.5)-CH_3(1.5)}$ ,  $\Delta^{CH_3(1.5)-CH_2(2)}$  and  $\Delta^{CH_2(2)-CH_2(2)}$  are needed for 2-methyl-butane. For 3-methyl-pentane  $N = 2$  for two  $CH_3$  groups at the end of the main chain,  $N' = 1$  for the other  $CH_3$  group and  $n = 3$  and  $\Delta^{CH_3(2)-CH_3(2)}$ ,  $\Delta^{CH_3(2)-CH_3(1)}$ ,  $\Delta^{CH_3(1)-CH_3(1)}$ ,  $\Delta^{CH_3(2)-CH_2(3)}$ ,  $\Delta^{CH_3(1)-CH_2(3)}$  and  $\Delta^{CH_2(3)-CH_2(3)}$  are needed.

The universal functions for the saturated molar volume and the vapor pressure of liquid alkanes,  $V^{ref}$  and  $p^{ref}$ , are determined from the observed thermodynamic data of propane [13] with the intermolecular potential parameters  $\varepsilon$  and  $\sigma$  in the literature [14] (See Appendix B).

$$\hat{V}^{ref} = 0.6019 + 0.5093\hat{T} + 3.948 \times 10^{-4} \exp(5.137\hat{T}) \quad (21)$$

$$\log_{10} \hat{p}^{ref} = 1.458 - 3.187/\hat{T} - 0.3761/\hat{T}^2 \quad (22)$$

The values of the inter-group potential parameters  $\varepsilon^{lm}$  and  $\sigma^{lm}$  and the distance correction parameter  $\Delta^{lm}$  ( $l$  and  $m = CH_3, CH_2$  and  $CH$ ) for liquid alkanes except for methane and ethane are determined such that the saturated molar volume and the vapor pressure are correlated with Eqs. (21) and (22) with the least squares method. Methane and ethane have just  $CH_4$  and  $CH_3$  groups, respectively, and do not have  $CH_2$  group. Thus, the values of the inter-group parameters  $\varepsilon^{CH_4-CH_4}$ ,  $\sigma^{CH_4-CH_4}$ ,  $\varepsilon^{CH_3-CH_3}$  and  $\sigma^{CH_3-CH_3}$  for methane and ethane are determined such that the saturated molar volume and the vapor pressure of methane and ethane are correlated with Eqs. (21) and (22).

The vapor pressure varies over several orders, thus it was evaluated in logarithm for the determination of the parameters. The values of  $\varepsilon^{lm}$  and  $\sigma^{lm}$  are shown in Table 1 and those of  $\Delta^{lm}$  are in Table 2. The value of  $\varepsilon^{CH_2-CH_2}$  is much smaller than that of  $\varepsilon^{CH_3-CH_2}$ , which suggests that the interaction between groups  $CH_2$ s might be much weaker than

that between groups  $\text{CH}_3$  and  $\text{CH}_2$ .

## 5. Corresponding states correlations of molar volume, vapor pressure and surface tension for liquid alkanes

### 5.1. Correlations with distance correction parameter

The molar volume and the vapor pressure are correlated well in the corresponding states with the inter-group potential parameters  $\epsilon^{lm}$  and  $\sigma^{lm}$  and the distance correction parameter  $\Delta^{lm}$  for n- and i-alkanes [13] and fall on the universal functions 21 and 22 as shown in Figs. 2 and 3, respectively. The universal function 21 gives the equation for the mixing molar volume of liquid alkanes in our another report [15].

Fig. 4 shows that the surface tension [13] is correlated satisfactorily in the corresponding states with the parameters determined above. The reduced surface tension is expressed by Eq. (23).

$$\hat{\gamma} = 3.711 - 3.932\hat{T} - 0.8873\hat{T}^2 \quad (23)$$

The root mean square deviations (RMSD) of the corresponding states correlations of the thermodynamic properties are shown in Table 3. As shown in the last section the vapor pressure was evaluated in logarithm, thus the RMSD is also evaluated in logarithm (in  $\log_{10} p$ ).

### 5.2. Comparison of corresponding states correlations with the use of inter-group potential to those with the use of intermolecular potential

The intermolecular potential parameters of the alkanes  $\epsilon$  and  $\sigma$  can be determined such that the molar volume and the vapor pressure reduced by Eqs. (17) and (18) without the inter-group potential parameters are expressed by the reference functions

Eqs. (21) and (22). The values of  $\varepsilon$  and  $\sigma$  determined in this manner are shown in Table 4. Figs. 5 and 6 show the corresponding states correlations for the molar volume and the vapor pressure with  $\varepsilon$  and  $\sigma$  determined here. The reduced thermodynamic properties with the intermolecular potential parameters are scattered in Figs. 5 and 6, while those with the inter-group potential parameters fall on the reference curves in Figs. 2 and 3. It is because  $\varepsilon$  and  $\sigma$  determined by Eqs. (7) and (8) with the inter-group potential parameters  $\varepsilon^{lm}$  and  $\sigma^{lm}$  weakly depend on temperature through the characteristic length  $d$ . RMSDs with the use of the intermolecular potential parameters are larger than those with the use of the inter-group potential parameters and the distance correction parameters as shown in Table 3.

### 5.3. Correlations with functions of distance correction parameter

The distance correction parameters  $\Delta^{lm}$ s can be expressed by functions of the location and the number of the functional groups in a molecule for the easiness with use and the prediction of the thermodynamic properties for the heavier alkanes. For n-alkanes  $\Delta^{CH3-CH3}$ ,  $\Delta^{CH3-CH2}$  and  $\Delta^{CH2-CH2}$  are expressed by the following equations.

$$\Delta^{CH3(N)-CH3(N)} = 2.885 \times 10^{-11} - 1.489 \times 10^{-10} \ln(2N-1.993) \quad [\text{m}], \quad N \geq 1 \quad (24)$$

$$\Delta^{CH3(N)-CH2} = 3.315 \times 10^{-10} - 1.031 \times 10^{-10} \exp(-0.3042N^2) - 1.965 \times 10^{-10} \ln(N+2.655) \quad [\text{m}],$$

$$N \geq 1 \quad (25)$$

$$\Delta^{CH2-CH2} = 0 \quad (26)$$

The number of the group  $\text{CH}_2$   $n$  is uniquely determined by the location of the group  $\text{CH}_3$   $N$  in n-alkanes, thus  $n$  is not included in Eq. (25).

For i-alkanes,  $\Delta^{CH3-CH3}$ ,  $\Delta^{CH3-CH2}$  ( $=\Delta^{CH3-CH}$ ) and  $\Delta^{CH2-CH2}$  ( $=\Delta^{CH2-CH}=\Delta^{CH-CH}$ ) are expressed by Eqs. (27) to (29).

$$\Delta^{CH3(N)-CH3(N')} = 3.202 \times 10^{-10} - 2.261 \times 10^{-10} \ln[2.551 + N + N' + 1.1(N-N')]$$

$$=3.202 \times 10^{-10} - 2.261 \times 10^{-10} \ln(2.551 + 2.1N - 0.1N^2) \quad [\text{m}], \quad N \geq N^* \quad (27)$$

$$\Delta^{CH_3(N)-CH_2(n)} = 3.340 \times 10^{-10} - 1.870 \times 10^{-10} \ln(N + 1.578 + 0.4209m + 0.085m^2) \\ - 1.230 \times 10^{-10} \exp[-1.81(N - 0.0925m^2 + 1.11m - 2.555)] \quad [\text{m}] \quad (28)$$

$$\Delta^{CH_2(n)-CH_2(n)} = -2.687 \times 10^{-11} + 1.345 \times 10^{-10} \ln(n + 0.1424) \quad [\text{m}] \quad (29)$$

where

$$m = \frac{n+1}{2} - N + 2 \quad (30)$$

$N$  and  $N^*$  are the locations of the group  $\text{CH}_3$ . For example, in case of 3-methyl-hexane  $N$  and  $N^* = 2.5$  and  $1.5$  for Eq. (27),  $N=2.5$  and  $1.5$  for Eq. (28) and  $n=4$  for Eqs. (28) and (29).

Figs. 7 to 9 show the corresponding states of the molar volume, the vapor pressure and the surface tension with the inter-group potential parameters  $\varepsilon^{lm}$  and  $\sigma^{lm}$  and the functions of the distance correction parameter  $\Delta^{lm}$  for alkanes. The molar volume and the vapor pressure are correlated well and the surface tension is correlated satisfactorily. RMSDs with the distance correction functions are a little larger than those with the distance correction parameter values as shown in Table 3.

#### 5.4. Corresponding States Correlations for Heavier Alkanes

The corresponding states correlations are applied to the thermodynamic properties of heavier liquid alkanes n-C<sub>22</sub> to n-C<sub>30</sub>, n-C<sub>32</sub> and n-C<sub>36</sub>, the data of which are available in the literature [13], with the use of the inter-group potential parameters  $\varepsilon^{lm}$  and  $\sigma^{lm}$  and the functions of the distance correction parameter  $\Delta^{lm}$  Eqs. (24) to (26), which are determined with the data of the thermodynamic properties of the lighter liquid alkanes. The RMSDs shown in Table 3 are a little larger than those for the lighter alkanes. However, Fig. 10 shows that the reduced molar volume and the vapor pressure almost

fall on the reference curves Eqs. (21) and (22), respectively, except at the high and low reduced temperatures. It can be said that the corresponding states equations, Eqs. (21) and (22), can estimate the molar volume and the vapor pressure of the heavier liquid alkanes with the mean deviations about 5 and 6 %, respectively.

The correlation can be extended and applied to the liquid alkane mixtures. The mixing molar volume is correlated with the parameters determined for the pure compounds without any binary interaction parameters specific to each mixture in our another report [15].

## **6. Conclusion**

The molar volume and the vapor pressure of the saturated liquid n-alkanes up to n-C<sub>21</sub> and i-alkanes up to i-C<sub>10</sub> are correlated in the corresponding states with the use of the inter-group potential parameters and the distance correction parameters better than with the use of the intermolecular potential parameters without the inter-group potential parameters. The distance correction parameter can account for the location of CH<sub>3</sub> group in the isomers and can express their thermodynamic properties. The surface tension is also correlated with the inter-group potential parameters and the distance correction parameters satisfactorily.

The distance correction parameters can be expressed by the functions of the location and the number of the functional groups in a molecule, with which the thermodynamic properties of the liquid alkanes up to n-C<sub>21</sub> and i-C<sub>10</sub> are correlated well and those of the heavier liquid alkanes n-C<sub>22</sub> to n-C<sub>30</sub>, n-C<sub>32</sub> and n-C<sub>36</sub>, which are not used for the determination of the parameters and the functions, are correlated satisfactorily.

## **7. List of symbols**

$A$	Helmholtz free energy
$d$	characteristic length
$d^{lm}$	distance between functional groups $l$ and $m$ when the separation distance between the molecules is $d$
$f$	Mayer $f$ bond
$f^b$	$f^b$ bond (blip function)
$g$	radial distribution function
$k$	Boltzmann's constant
$N, N'$	location of functional group
$n$	number of functional group
$N_A$	Avogadro number
$p$	vapor pressure
$r$	separation distance
$r_m$	separation distance at which intermolecular potential takes the minimum value
$T$	absolute temperature
$V$	molar volume
$v$	intermolecular potential
$w$	attractive potential

### 7.1. Greek letters

$\beta$	reciprocal temperature ( $=1/kT$ )
$\gamma$	surface tension
$\Delta^{lm}$	distance correction parameter between functional groups $l$ and $m$
$\varepsilon$	intermolecular potential parameter
$\varepsilon^{lm}$	inter-group potential parameter (potential parameter between functional groups)

	$l$ and $m$ )
$\sigma$	intermolecular potential parameter
$\sigma^{lm}$	inter-group potential parameter (potential parameter between functional groups $l$ and $m$ )
$\phi$	inter-group potential (potential between functional groups)

## 7.2. Subscript

$i, j$	molecule
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## 7.3. Superscripts

$ex$	excess
$hs$	hard sphere
$l, m$	functional group
$ref$	reference
$\wedge$	reduced form
0	repulsive potential

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## Appendix A

The reduced excess Helmholtz free energy of a system is expressed in terms of diagrams [16].

$$-\hat{A}^{ex} = -\beta A^{ex} = [\text{sum of all simple irreducible diagrams composed of two or more black density circles and } f \text{ bonds}] = [ \bullet \text{---} \bullet + \text{triangle} + \text{square} + \text{square with diagonal} + \dots ] \quad (\text{A1})$$

Here the dot is a black circle and the segment line is an  $f$  bond defined by Eq. (A2).

$$f = \exp(-\beta v) - 1 \quad (\text{A2})$$

The  $f$  bond is separated into  $f^{ref}$  bond for the reference system and  $f^b$  bond which was called the blip function by Andersen et al. [17] The  $f^b$  bond is nonzero only in a small range of the molecular separation.

$$f = f^{ref} + f^b \quad (\text{A3})$$

$$f^{ref} = \exp(-\beta v^{ref}) - 1 \quad (\text{A4})$$

Introduction of Eq. (A3) into Eq. (A1) yields

$$-\beta A^{ex} = -\beta A^{ex ref} + [ \bullet \cdots \bullet + \text{triangle with dotted bond} + \text{square with dotted bond} + \text{square with diagonal and dotted bond} + \dots ] + [\text{higher order perturbation terms with respect to } f^b] \quad (\text{A5})$$

where the dotted bond represents the  $f^b$  bond. If the second square-bracketed terms of higher orders are neglected and the characteristic length  $d$  is chosen such that the sum of the diagrams involving only one  $f^b$  bond vanishes, the excess free energy is expressed by Eq. (A6).

$$\hat{A}^{ex} = \beta A^{ex} = \beta A^{ex,ref} = \hat{A}^{ex,ref} \quad (A6)$$

The radial distribution function for molecules 1 and 2, the position of which are  $r_1$  and  $r_2$ , is expanded by a series of diagrams [16].

$$g(1,2) = \left[ \text{Diagram 1} \right] * \left[ \text{Diagram 2} + \text{Diagram 3} + \text{Diagram 4} + \text{Diagram 5} + \dots \right] \quad (A7)$$

where  $=$  is the  $e$  bond,  $\exp(-\beta v)$ .

The characteristic length  $d$  is determined such that the first bracketed term in Eq. (A5) vanishes. From the first bracketed term in Eq. (A5) and Eq. (A7),  $d$  value is given implicitly as

$$\int g_{ij} \exp(\beta v_{ij}) f^b_{ij} d\vec{r} = 0 \quad (A8)$$

where

$$f^b_{ij} = \exp(-\beta v_{ij}) - \exp(-\beta v_{ij}^{ref}) \quad (A9)$$

Eq. (A8) has the blip function which is effectively nonzero only in the vicinity of  $r = d$ . On the contrary,  $g(r)$  is not sensitive to  $r$  in this range and it may be assumed that  $g(r)$  is constant irrespective of  $r$ . This assumption yields

$$d^3 / 3 = \int_d^\infty [\exp(\beta v^0) - 1] r^2 dr \quad (A10)$$

## Appendix B

Propane is used for the determination of the universal functions of the molar volume and the vapor pressure because it has a larger reduced temperature range for the liquid state than all the other alkanes investigated and it is the smallest molecule that has both groups  $\text{CH}_3$  and  $\text{CH}_2$ . The observed molar volume and vapor pressure of propane [13] are reduced by Eqs. (17) and (18) with the characteristic parameters  $d$  and  $\varepsilon$ , where  $d$  is evaluated by Eq. (16) with the intermolecular potential parameters  $\varepsilon$  and  $\sigma$  in the

literature [14]. The reduced thermodynamic properties are fitted by Eqs. (21) and (22) in the text, which are the universal functions.

The values of the inter-group potential parameters for n-alkane  $\epsilon^{lm}$  and  $\sigma^{lm}$  ( $l$  and  $m = \text{CH}_3, \text{CH}_2$  and  $\text{CH}$ ) are determined such that the molar volume and the vapor pressure reduced with the parameters  $d$  and  $\epsilon$  are correlated in the corresponding states with Eqs. (21) and (22) for propane, n-butane and n-pentane [13] with the least squares method. The values for i-alkane are determined such that the thermodynamic properties are correlated for i-butane, i-pentane and i-hexanes [13] in a similar manner. Methane and ethane have just  $\text{CH}_4$  and  $\text{CH}_3$  groups, respectively, and do not have  $\text{CH}_2$  group. Thus, the values of the inter-group parameters  $\epsilon^{\text{CH}_4-\text{CH}_4}$ ,  $\sigma^{\text{CH}_4-\text{CH}_4}$ ,  $\epsilon^{\text{CH}_3-\text{CH}_3}$  and  $\sigma^{\text{CH}_3-\text{CH}_3}$  for methane and ethane are determined such that the molar volume and the vapor pressure of methane and ethane are correlated with Eqs. (21) and (22).

The values of the distance correction parameter  $\Delta^{lm}$  are determined such that the molar volume and the vapor pressure are correlated with Eqs. (21) and (22). The molecular size of methane and ethane is small and their shape is almost sphere, thus the distance correction parameters  $\Delta^{\text{CH}_4-\text{CH}_4}$  and  $\Delta^{\text{CH}_3-\text{CH}_3}$  for methane and ethane are set to be zero.

The procedure for the correlations is as follows. (i) The approximate intermolecular potential parameters  $\epsilon'$  and  $\sigma'$  are evaluated from Eqs. (7) and (8) with the inter-group potential parameters  $\epsilon^{lm}$  and  $\sigma^{lm}$  without  $\Delta^{lm}$ . (ii) The approximate characteristic length  $d'$  is evaluated from Eq. (16) with  $\epsilon'$  and  $\sigma'$ . (iii) Eqs. (7) and (8) with  $\epsilon^{lm}$ ,  $\sigma^{lm}$ ,  $d'$  and the distance correction parameter  $\Delta^{lm}$  give the desired intermolecular potential parameters  $\epsilon$  and  $\sigma$ , (iv) with which Eq. (16) gives the desired characteristic length  $d$ . (v) Finally the observed values of the molar volume and the vapor pressure are reduced with  $d$  and  $\epsilon$  and are correlated with the reduced temperature Eq. (20).

An example of the procedure for the molar volume of propane at 250K is shown below.

(i) A molecule of propane has two CH<sub>3</sub> and one CH<sub>2</sub> functional groups. Thus, there are four CH<sub>3</sub>-CH<sub>3</sub>, four CH<sub>3</sub>-CH<sub>2</sub> and one CH<sub>2</sub>-CH<sub>2</sub> functional group interactions between the two molecules. From Eqs. (7) and (8) in the text with  $\varepsilon^{CH_3-CH_3}$ ,  $\varepsilon^{CH_3-CH_2}$ ,  $\varepsilon^{CH_2-CH_2}$ ,  $\sigma^{CH_3-CH_3}$ ,  $\sigma^{CH_3-CH_2}$  and  $\sigma^{CH_2-CH_2}$  in Table 1 without  $\Delta^{lm}$ , the approximate intermolecular potential parameters  $\varepsilon'$  and  $\sigma'$  are evaluated.

$$\varepsilon' = \frac{\left[ 4 \times 1.0580 \times 10^{-22} \times (5.2574 \times 10^{-10})^6 + 0.063597 \times 10^{-22} \times (8.2883 \times 10^{-10})^6 \right]^2}{\left[ 4 \times 1.0580 \times 10^{-22} \times (5.2574 \times 10^{-10})^{12} + 0.063597 \times 10^{-22} \times (8.2883 \times 10^{-10})^{12} \right]} + \frac{4 \times 42.810 \times 10^{-22} \times (3.7542 \times 10^{-10})^6}{\left[ 4 \times 1.0580 \times 10^{-22} \times (5.2574 \times 10^{-10})^{12} + 0.063597 \times 10^{-22} \times (8.2883 \times 10^{-10})^{12} \right]}$$

$$= 35.887 \times 10^{-22} \text{ J}$$

$$\sigma' = \left[ \frac{4 \times 1.0580 \times 10^{-22} \times (5.2574 \times 10^{-10})^{12} + 0.063597 \times 10^{-22} \times (8.2883 \times 10^{-10})^{12}}{4 \times 1.0580 \times 10^{-22} \times (5.2574 \times 10^{-10})^6 + 0.063597 \times 10^{-22} \times (8.2883 \times 10^{-10})^6} + \frac{4 \times 42.810 \times 10^{-22} \times (3.7542 \times 10^{-10})^{12}}{4 \times 1.0580 \times 10^{-22} \times (5.2574 \times 10^{-10})^6 + 0.063597 \times 10^{-22} \times (8.2883 \times 10^{-10})^6} \right]^{1/6}$$

$$= 5.0538 \times 10^{-10} \text{ m}$$

(ii) From Eq. (16) with the  $\varepsilon'$  and  $\sigma'$  values obtained, the approximate characteristic length  $d'$  is

$$d' = 5.0538 \times 10^{-10} \times \{ 0.9573 + 5.020 \times 10^{-2} \times \ln[35.887 \times 10^{-22} / (1.3807 \times 10^{-23} \times 250)] - 5.157 \times 10^{-3} \times [35.887 \times 10^{-22} / (1.3807 \times 10^{-23} \times 250)] \}$$

$$= 4.8208 \times 10^{-10} \text{ m}$$

(iii) From Eqs. (7) and (8) with  $\varepsilon^{CH_3-CH_3}$ ,  $\varepsilon^{CH_3-CH_2}$ ,  $\varepsilon^{CH_2-CH_2}$ ,  $\sigma^{CH_3-CH_3}$ ,  $\sigma^{CH_3-CH_2}$  and  $\sigma^{CH_2-CH_2}$  in Table 1,  $\Delta^{CH_3(1)-CH_3(1)}$ ,  $\Delta^{CH_3(1)-CH_2(1)}$  and  $\Delta^{CH_2(1)-CH_2(1)}$  in Table 2 or Eqs. (24) through (26) ( $N=1$ ) and the  $d'$  value obtained, the desired intermolecular potential

parameters  $\varepsilon$  and  $\sigma$  are

$$\varepsilon = \frac{\left[ \begin{aligned} &4 \times 1.0580 \times 10^{-22} \times \left( \frac{5.2574 \times 10^{-10}}{4.8208 \times 10^{-10} - 0.24517 \times 10^{-10}} \right)^6 \\ &+ 0.063597 \times 10^{-22} \times \left( \frac{8.2883 \times 10^{-10}}{4.8208 \times 10^{-10} + 0.099815 \times 10^{-10}} \right)^6 \\ &+ 4 \times 42.810 \times 10^{-22} \times \left( \frac{3.7542 \times 10^{-10}}{4.8208 \times 10^{-10} + 0.051675 \times 10^{-10}} \right)^6 \end{aligned} \right]^2}{\left[ \begin{aligned} &4 \times 1.0580 \times 10^{-22} \times \left( \frac{5.2574 \times 10^{-10}}{4.8208 \times 10^{-10} - 0.24517 \times 10^{-10}} \right)^{12} \\ &+ 0.063597 \times 10^{-22} \times \left( \frac{8.2883 \times 10^{-10}}{4.8208 \times 10^{-10} + 0.099815 \times 10^{-10}} \right)^{12} \\ &+ 4 \times 42.810 \times 10^{-22} \times \left( \frac{3.7542 \times 10^{-10}}{4.8208 \times 10^{-10} + 0.051675 \times 10^{-10}} \right)^{12} \end{aligned} \right]} \\ = 35.047 \times 10^{-22} \text{ J} \\ \sigma = \frac{\left[ \begin{aligned} &4 \times 1.0580 \times 10^{-22} \times \left( \frac{5.2574 \times 10^{-10}}{4.8208 \times 10^{-10} - 0.24517 \times 10^{-10}} \right)^{12} \\ &+ 0.063597 \times 10^{-22} \times \left( \frac{8.2883 \times 10^{-10}}{4.8208 \times 10^{-10} + 0.099815 \times 10^{-10}} \right)^{12} \\ &+ 4 \times 42.810 \times 10^{-22} \times \left( \frac{3.7542 \times 10^{-10}}{4.8208 \times 10^{-10} + 0.051675 \times 10^{-10}} \right)^{12} \end{aligned} \right]^{1/6}}{\left[ \begin{aligned} &4 \times 1.0580 \times 10^{-22} \times \left( \frac{5.2574 \times 10^{-10}}{4.8208 \times 10^{-10} - 0.24517 \times 10^{-10}} \right)^6 \\ &+ 0.063597 \times 10^{-22} \times \left( \frac{8.2883 \times 10^{-10}}{4.8208 \times 10^{-10} + 0.099815 \times 10^{-10}} \right)^6 \\ &+ 4 \times 42.810 \times 10^{-22} \times \left( \frac{3.7542 \times 10^{-10}}{4.8208 \times 10^{-10} + 0.051675 \times 10^{-10}} \right)^6 \end{aligned} \right]} \times 4.8208 \times 10^{-10} \\ = 5.0628 \times 10^{-10} \text{ m}$$

(iv) From Eq. (16) with the  $\varepsilon$  and  $\sigma$  values obtained, the desired characteristic length  $d$  is

$$\begin{aligned} d &= 5.0628 \times 10^{-10} \times \{0.9573 + 5.020 \times 10^{-2} \times \ln[35.047 \times 10^{-22} / (1.3807 \times 10^{-23} \times 250)] \\ &\quad - 5.157 \times 10^{-3} \times [35.047 \times 10^{-22} / (1.3807 \times 10^{-23} \times 250)]\} \\ &= 4.8240 \times 10^{-10} \text{ m} \end{aligned}$$

(v) From Eq. (20) with the  $d$  and  $\varepsilon$  values obtained, the reduced temperature  $\hat{T}$  is

$$\hat{T} = \frac{1.3807 \times 10^{-23} \times 250}{35.047 \times 10^{-22}} = 0.98486$$

From Eq. (17) with the  $d$  value, the reduced molar volume for observed value  $\hat{V}_{obs}$  is

$$\hat{V}_{obs} = \frac{7.885 \times 10^{-4}}{6.02205 \times 10^{23} \times (4.8240 \times 10^{-10})^3} = 1.1663$$

From Eq. (21) with the  $\hat{T}$  value, the reduced molar volume for calculated value  $\hat{V}_{calc}$  is

$$\hat{V}_{calc} = 0.6019 + 0.5093 \times 0.98486 + 3.948 \times 10^{-4} \exp(5.137 \times 0.98486) = 1.1656$$

**Table 1. Inter-group potential parameters  $\varepsilon^{lm}$  and  $\sigma^{lm}$  for n- and i-alkanes**

pair of groups	$\varepsilon^{lm} \times 10^{22} [\text{J}]$	$\sigma^{lm} \times 10^{10} [\text{m}]$
$l-m$		
n-alkane		
CH <sub>4</sub> -CH <sub>4</sub> (methane)	17.737	3.9844
CH <sub>3</sub> -CH <sub>3</sub> (ethane)	7.1867	4.5697
CH <sub>3</sub> -CH <sub>3</sub>	1.0580	5.2574
CH <sub>3</sub> -CH <sub>2</sub>	42.810	3.7542
CH <sub>2</sub> -CH <sub>2</sub>	0.063597	8.2883
i-alkane		
CH <sub>3</sub> -CH <sub>3</sub>	1.2377	5.7364
CH <sub>3</sub> -CH <sub>2</sub> , CH <sub>3</sub> -CH	44.000	3.6648
CH <sub>2</sub> -CH <sub>2</sub> , CH <sub>2</sub> -CH, CH-CH	0.073800	8.6892

**Table 2. Distance correction parameter  $\Delta^{lm}$  for n- and i-alkanes**

n-alkane					
$N$	$\Delta^{CH3(N)-CH3(N)} \times 10^{10} [\text{m}]$	$N-n$	$\Delta^{CH3(N)-CH2(n)} \times 10^{10} [\text{m}]$	$n$	$\Delta^{CH2(n)-CH2(n)} \times 10^{10} [\text{m}]$
0	0	0-0	0	0	0
0.5	0	0.5-0	0	1	0.099815
1	-0.24517	1-1	0.051675	2	0.013119
1.5	-0.41849	1.5-2	0.0055029	3	0.39447
2	-1.2947	2-3	0.092679	4	0.31665
2.5	-1.6261	2.5-4	-0.031489	5	0.37981
3	-1.9540	3-5	-0.15852	6	0.27928
3.5	-2.2014	3.5-6	-0.29475	7	0.25035
4	-2.4341	4-7	-0.43027	8	0.32173
4.5	-2.6813	4.5-8	-0.61261	9	0.12492
5	-2.8192	5-9	-0.68732	10	0.10882
5.5	-2.9858	5.5-10	-0.80474	11	0.26498
6	-3.1574	6-11	-0.94933	12	0.15608
6.5	-3.2863	6.5-12	-1.0439	13	-0.16546
7	-3.3969	7-13	-1.1156	14	-0.074273
7.5	-3.5235	7.5-14	-1.2258	15	-0.11958
8	-3.6330	8-15	-1.3160	16	-0.15490
8.5	-3.7354	8.5-16	-1.4007	17	-0.36718
9	-3.8261	9-17	-1.4634	18	-0.22700
9.5	-3.9268	9.5-18	-1.5698	19	-0.15462
10	-4.0197	10-19	-1.6672		



i-alkane

$N-N'$	$\Delta^{CH3(N)-CH3(N')} \times 10^{10}[\text{m}]$	$N-n$	$\Delta^{CH3(N)-CH2(n)} \times 10^{10}[\text{m}]$	$n$	$\Delta^{CH2(n)-CH2(n)} \times 10^{10}[\text{m}]$
1-1	-0.22916	1-1	0.14077	1	0.48803
1.5-1.5	-0.65751	1.5-2	0.32929	2	0.10603
2-2	-1.0597	2-3	0.28509	3	2.1421
2.5-2.5	-1.3690	2.5-4	0.18075	4	1.8671
3-3	-1.6498	3-5	0.045276	5	2.4598
3.5-3.5	-1.9003	3.5-6	-0.10281	6	2.9119
4-4	-2.1235	4-7	-0.23968	7	2.9237
1-2	-1.1085	1-3	0.23429		
1.5-2.5	-1.3939	1.5-4	0.19721		
2-3	-1.6921	2-5	0.031083		
2.5-3.5	-1.9526	2.5-6	-0.11039		
3-4	-2.1586	3-7	-0.23294		
1-3	-1.7075	1-5	-0.010576		
1.5-3.5	-1.9611	1.5-6	-0.14924		
2-4	-2.1854	2-7	-0.26951		
1-4	-2.1854	1-7	-0.30352		

**Table 3. Root mean square deviations of corresponding states correlations for thermodynamic properties of liquid n-alkanes C<sub>1</sub> to n-C<sub>21</sub>, i-alkanes i-C<sub>4</sub> to i-C<sub>10</sub> and heavier n-alkanes n-C<sub>22</sub> to n-C<sub>36</sub> [%]**

	with $\Delta^{lm}$ value <sup>1)</sup>	with $\Delta^{lm}$ function <sup>2)</sup>	with $\varepsilon$ and $\sigma$ <sup>3)</sup>
molar volume			
C <sub>1</sub> to n-C <sub>21</sub>	1.932	2.031	5.348
i-C <sub>4</sub> to i-C <sub>10</sub>	1.790	2.054	2.275
average	1.861	2.042	3.812
n-C <sub>21</sub> to n-C <sub>36</sub>	-	5.046	-
vapor pressure <sup>4)</sup>			
C <sub>1</sub> to n-C <sub>21</sub>	3.020	3.394	13.44
i-C <sub>4</sub> to i-C <sub>10</sub>	2.035	2.266	12.00
average	2.527	2.830	12.72
n-C <sub>21</sub> to n-C <sub>36</sub>	-	5.897	-
surface tension			
C <sub>1</sub> to n-C <sub>21</sub>	24.46	24.35	30.74
i-C <sub>4</sub> to i-C <sub>10</sub>	19.87	22.97	37.24
average	22.17	23.66	33.99
n-C <sub>21</sub> to n-C <sub>36</sub>	-	28.24	-

1) with the use of inter-group potential parameters  $\varepsilon^{lm}$  and  $\sigma^{lm}$  and distance correction parameter  $\Delta^{lm}$  values

2) with the use of inter-group potential parameters  $\varepsilon^{lm}$  and  $\sigma^{lm}$  and distance correction

parameter  $\Delta^{lm}$  functions

- 3) with the use of intermolecular potential parameters  $\varepsilon$  and  $\sigma$  shown in Table A1
- 4) RMSD for vapor pressure is evaluated in  $\log_{10} p$ .

**Table 4. Intermolecular potential parameters  $\varepsilon$  and  $\sigma$  for n- and i-alkanes**

	$\varepsilon \times 10^{21}[\text{J}]$	$\sigma \times 10^{10}[\text{m}]$		$\varepsilon \times 10^{21}[\text{J}]$	$\sigma \times 10^{10}[\text{m}]$
methane	1.7737	3.9844	2-methylpropane	3.8999	5.4986
ethane	2.8747	4.5697	2-methylbutane	4.4057	5.8354
propane	3.5045	5.0627	2-methylpentane	4.7511	6.1647
n-butane	4.0522	5.4745	3-methylpentane	4.8295	6.1413
n-pentane	4.5021	5.8417	2-methylhexane	5.1157	6.4660
n-hexane	4.9066	6.1689	3-methylhexane	5.2386	6.4480
n-heptane	5.2098	6.4649	2-methylheptane	5.4233	6.7403
n-octane	5.5562	6.7594	3-methylheptane	5.4984	6.7240
n-nonane	5.8061	7.0149	4-methylheptane	5.4644	6.7192
n-decane	6.0928	7.3369	2-methyloctane	5.7180	7.0129
n-undecane	6.4093	7.5375	3-methyloctane	5.6477	6.9802
n-dodecane	6.6565	7.7773	4-methyloctane	5.7063	6.9783
n-tridecane	6.8559	8.0166	2-methylnonane	5.9429	7.2566
n-tetradecane	7.0737	8.2224	3-methylnonane	5.9604	7.2225
n-pentadecane	7.4941	8.4525	4-methylnonane	5.8913	7.2271
n-hexadecane	7.6044	8.6473	5-methylnonane	5.9387	7.2306
n-heptadecane	7.8127	8.8421			
n-octadecane	8.0321	9.0361			
n-nonadecane	8.3960	9.2218			
n-eicosane	8.4993	9.4112			
n-heneicosane	8.7074	9.6024			

### Figure captions

**Fig. 1.** Schematic diagram of characteristic length  $d$  and inter-group distance  $d^{lm}$  for propane. Dashed line is  $d$ , dot line is  $d^{CH3-CH3} = d + \Delta^{CH3-CH3}$ , dashed-dot line is  $d^{CH3-CH2} = d + \Delta^{CH3-CH2}$  and dashed-two dot line is  $d^{CH2-CH2} = d + \Delta^{CH2-CH2}$ .

**Fig. 2.** Corresponding states correlation of molar volume for (a) n-alkanes and (b) i-alkanes with inter-group potential parameters  $\varepsilon^{lm}$  and  $\sigma^{lm}$  and distance correction parameter  $\Delta^{lm}$ .

**Fig. 3.** Corresponding states correlation of vapor pressure for (a) n-alkanes and (b) i-alkanes with inter-group potential parameters  $\varepsilon^{lm}$  and  $\sigma^{lm}$  and distance correction parameter  $\Delta^{lm}$ . The symbols are the same as in Fig. 2.

**Fig. 4.** Corresponding states correlation of surface tension for (a) n-alkanes and (b) i-alkanes with inter-group potential parameters  $\varepsilon^{lm}$  and  $\sigma^{lm}$  and distance correction parameter  $\Delta^{lm}$ . The symbols are the same as in Fig. 2.

**Fig. 5.** Corresponding states correlation of molar volume for (a) n-alkanes and (b) i-alkanes with intermolecular potential parameters  $\varepsilon$  and  $\sigma$ . The symbols are the same as in Fig. 2.

**Fig. 6.** Corresponding states correlation of vapor pressure for (a) n-alkanes and (b) i-alkanes with intermolecular potential parameters  $\varepsilon$  and  $\sigma$ . The symbols are the same as in Fig. 2.

**Fig. 7.** Corresponding states correlation of molar volume for (a) n-alkanes and (b) i-alkanes with inter-group potential parameters  $\varepsilon^{lm}$  and  $\sigma^{lm}$  and functions of distance correction parameter  $\Delta^{lm}$ . The symbols are the same as in Fig. 2.

**Fig. 8.** Corresponding states correlation of vapor pressure for (a) n-alkanes and (b) i-alkanes with inter-group potential parameters  $\varepsilon^{lm}$  and  $\sigma^{lm}$  and functions of distance correction parameter  $\Delta^{lm}$ . The symbols are the same as in Fig. 2.

**Fig. 9.** Corresponding states correlation of surface tension for (a) n-alkanes and (b) i-alkanes with inter-group potential parameters  $\varepsilon^{lm}$  and  $\sigma^{lm}$  and functions of distance correction parameter  $\Delta^{lm}$ . The symbols are the same as in Fig. 2.

**Fig. 10.** Corresponding states correlations of molar volume and vapor pressure for heavier alkanes with inter-group potential parameters  $\varepsilon^{lm}$  and  $\sigma^{lm}$  and functions of distance correction parameter  $\Delta^{lm}$ .