SHORT COMMUNICATIONS

PREDICTION OF ACENTRIC FACTOR OF ALKANES BY THE GROUP CONTRIBUTION METHOD

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Acentric factor is one of the most useful and important values in calculating the physical properties of pure compounds as well as mixtures. It is also indispensable for the equation of states\(^{6,12}\).

Pitzer\(^{10,11}\) defined it as:
\[
\omega = -\log P_{vp}(at \ T_r=0.7) - 1.0
\]
where \(P_{vp}\) (at \(T_r=0.7\)) is the reduced vapor pressure at a reduced temperature of 0.7.

Edmister\(^1\) and Lee and Kesler\(^6\) proposed a useful estimation technique for the acentric factor, but they required the normal boiling point, the critical temperature and the critical pressure. The simple method proposed here is capable of predicting the acentric factors of alkanes by knowing only the chemical formula with reasonable accuracy.

1. Proposed Group Contribution Method

Among several empirical methods, the group contribution method has wide applicability for predicting the physical properties of pure compounds such as the standard heat of formation at 25°C\(^{14}\), the critical constant\(^7\), the liquid molar volume at 25°C\(^5\), the refractive index at 25°C\(^5\) and the latent heat of vaporization at the normal boiling point\(^3,4\).

The group contribution method is a convenient and useful tool for calculation of physical properties of pure compounds when there is no information except their chemical formula.

2. Determination of the Group Contribution

Acentic factors may contain four kinds of functional groups: \([-\text{CH}_3\text{]}, [-\text{CH}_2\text{}], [-\text{CH}\text{]}\) and \([-\text{C}\text{]}\). When an alkane has side chains which consist of 3 or more carbon atoms, correction is required. The values of these group increments and correction for side-chains were determined by data regression using experimental acentric factors. The recommended values for 59 alkanes (ethane to \(n\)-eicosane) by Passut and Danner\(^9\), and Henry and Danner\(^3\) were used as experimental data.

The group increments and correction for side-chains determined in this work are shown in Table 1. When the contribution of \([-\text{CH}\text{]}\) group is calculated, it is necessary to use the universal nomenclature adopted by IUPAC. This is because, the contribution of \([-\text{CH}\text{]}\) group has a different value depending on its position on the main chain of carbon atom of \([-\text{CH}\text{]}\) group.

3. Calculation of Acentric Factors and Results

Examples of calculations of acentric factors for \(n\)-octane and 2, 3, 4-tetramethylpentane are presented in Appendix. The calculated results for 59 alkanes (ethane to \(n\)-eicosane) were compared with those of experimental data and the error is sum-

\[\text{Table 1 Group contributions for calculation of acentric factor of alkanes}\]

<table>
<thead>
<tr>
<th>Increment</th>
<th>(\Delta\omega) [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-\text{CH}_3)</td>
<td>0.0460</td>
</tr>
<tr>
<td>(-\text{CH}_2)</td>
<td>(0.0527-0.0004n)n</td>
</tr>
<tr>
<td>(-\text{CH})</td>
<td>0.0410-0.0035(P-1)</td>
</tr>
<tr>
<td>(-\text{C})</td>
<td>-0.0141 (not adjacent to terminal carbon)</td>
</tr>
<tr>
<td>\text{[correction for side-chains]}</td>
<td></td>
</tr>
<tr>
<td>side-chains consist of 3 or more carbon atoms</td>
<td>-0.0264</td>
</tr>
</tbody>
</table>

[note] \(n\): total number of increments in a molecule
\(P\): position number of carbon atom on the main chain

1 Received April 17, 1981. Correspondence concerning this article should be addressed to D. Hoshino.
Table 2 Summary of errors in the calculation of acentric factor of alkanes

<table>
<thead>
<tr>
<th>Range of errors E* [%]</th>
<th>Number of compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Proposed method</td>
</tr>
<tr>
<td>0.0 &lt; E ≤ 1.0</td>
<td>19</td>
</tr>
<tr>
<td>1.0 &lt; E ≤ 2.0</td>
<td>13</td>
</tr>
<tr>
<td>2.0 &lt; E ≤ 3.0</td>
<td>6</td>
</tr>
<tr>
<td>3.0 &lt; E ≤ 4.0</td>
<td>10</td>
</tr>
<tr>
<td>4.0 &lt; E ≤ 5.0</td>
<td>5</td>
</tr>
<tr>
<td>5.0 &lt; E ≤ 6.0</td>
<td>6</td>
</tr>
<tr>
<td>6.0 &lt; E ≤ 10.0</td>
<td>0</td>
</tr>
<tr>
<td>10.0 &lt; E ≤ 50.0</td>
<td>0</td>
</tr>
<tr>
<td>50.0 &lt; E ≤ 100.0</td>
<td>0</td>
</tr>
<tr>
<td>100.0 &lt; E</td>
<td>0</td>
</tr>
<tr>
<td>(total)</td>
<td>59</td>
</tr>
</tbody>
</table>

Average error** [%] = \( \frac{\sum|\text{E true} - \text{E calc}|}{\sum N_{\text{comp}}} \)

Maximum error [%] = 21.0

Table 3 Summary of errors in the calculation of liquid densities of 5 alkanes

<table>
<thead>
<tr>
<th>Range of error E* [%]</th>
<th>Method I</th>
<th>Method II</th>
<th>Method III</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0 &lt; E ≤ 1.0</td>
<td>21</td>
<td>21</td>
<td>19</td>
</tr>
<tr>
<td>1.0 &lt; E ≤ 2.0</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>(total)</td>
<td>22</td>
<td>22</td>
<td>22</td>
</tr>
</tbody>
</table>

Average error** [%] = \( \frac{\sum|\rho_{\text{true}} - \rho_{\text{calc}}|}{\sum N_{\text{data points}}} \)

Maximum error [%] = 0.10, 0.10, 0.13

The calculated results were compared with those of experimental data\(^{(a)}\) (temperature ranging from 0°C to 30°C, 22 data) and the error is summarized in Table 3. The experimental values at 25°C were utilized for calculating the scaling volume. The calculated results were compared with those of experimental data and the error is summarized in Table 3. The relative average errors of Method I, Method II and Method III are 0.04%, 0.04% and 0.05%, respectively. The maximum errors are 0.10%, 0.01% and 0.13%, respectively.

The acentric factors had a very weak effect on the calculation of liquid densities by the Yamada and Gunn equation. For example, the acentric factor of 2, 2-dimethylpentane by the Macknick and Prausnitz vapor pressure equation is 25% different from the experimental value. But, using the same acentric factor, the liquid densities were calculated within 1.3% error.

Conclusions

Acentric factors of 59 alkanes (ethane to n-eicosane) were successfully predicted by the group contribution method. This method is very simple and requires only the knowledge of the chemical formula of the molecules. Judging from comparison between predicted and experimental values, it may be concluded that the proposed group contribution method is useful for prediction of acentric factors of alkanes when these are lacking in the literature.

Appendix

The use of the group increment of Table 1 is shown by calculating acentric factors of n-octane and 2, 3, 3, 4-tetramethylpentane.

\[ \omega = \sum \Delta \omega = \sum (-CH_2) + \sum (-CH_3) \]
\[ = (0.0460) \times 2 + (0.0527 - 0.0004 \times 6) \times 6 \]
\[ = -0.3938 \]

error: \( \frac{(0.3942 - 0.3938)/0.3942}{100} = 0.1 \text{ [%]} \)

2, 3, 3, 4-tetramethylpentane

\[ \frac{1}{2} \text{CH}_3 \quad \frac{1}{2} \text{CH}_3 \quad \frac{1}{2} \text{CH} \quad \frac{1}{2} \text{CH} \quad \text{CH}_3 \]

\[ \frac{1}{2} \text{CH}_3 \quad \frac{1}{2} \text{CH}_3 \quad \frac{1}{2} \text{CH}_3 \]

\[ \exp 0.2994^{(b)} \]

Liquid densities of 5 alkanes (2, 2-dimethylpentane, n-hexane, n-heptane, n-octane and n-nonane) were calculated with the following acentric factors:

Method I) experimentally obtained acentric factors

Method II) acentric factors obtained from proposed group contribution method

Method III) acentric factors obtained from the Macknick and Prausnitz vapor pressure equation

The acentric factors had a very weak effect on the calculation of liquid densities by the Yamada and Gunn equation. For example, the acentric factor of 2, 2-dimethylpentane by the Macknick and Prausnitz vapor pressure equation is 25% different from the experimental value. But, using the same acentric factor, the liquid densities were calculated within 1.3% error.

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\[ \frac{1}{2} \text{CH}_3 \quad \frac{1}{2} \text{CH}_3 \quad \frac{1}{2} \text{CH}_3 \]

\[ \exp 0.2994^{(b)} \]
\[
\omega = 2(-\text{CH}_2) + 2(-\text{CH}_-) + 2(-\text{C}_-) + \text{(side-chain correction)} \\
= (0.0460) \times 6 + [0.0410 - 0.0035(2 - 1)] + (0.0410 - 0.0035(4 - 1)) + (-0.0141) + (-0.0264) \\
= 0.3035 \\
\text{error: 1.4 } \% \]

Acknowledgement

The authors express their thanks to Hirohisa Nagashima for his assistance in the computational work.

Nomenclature

- \( E \) = relative error
- \( N_{\text{comp}} \) = number of compounds
- \( n \) = total number of increments in a molecule
- \( P \) = position number of carbon atom on the main chain
- \( P_{\text{spr}} \) = reduced vapor pressure
- \( T_e \) = reduced temperature
- \( \rho \) = liquid density \([\text{g/cm}^3]\)
- \( \omega \) = acentric factor
- \( \omega_{0,i} \) = increment of acentric factor of alkanes for \( i \)-th functional group

(Subscripts)

- \( \text{cal} \) = calculated
- \( \text{exp} \) = experimental

Literature Cited

5) \textit{idem}: ibid., 22, 218 (1979).

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VISCOSITY OF CHLORODIFLUOROMETHANE (R22) AT HIGH PRESSURES

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Introduction

Viscosity of fluids is one of the important thermophysical properties. An accurate knowledge of viscosity at high pressures serves to determine the interaction between molecules and is required in the design of various unit operations and equipment in chemical industries. Papers about the viscosities of polar gases at high pressures are very few. This paper presents accurate viscosity values of chlorodifluoromethane (R22), a highly polar gas, at pressures up to around the saturated vapor pressure of R22 below the critical temperature (369.2 K) of 298.15, 323.15 and 348.15 K, and up to 50 x 10^5 Pa at 373.15 K, by use of a precision oscillating-disk viscometer described in detail previously.\(^4,5\).

1. Experimental

The experimental procedure and the method of evaluating gas viscosity are almost the same as those described in the previous papers\(^4,5\) except for a suspension wire. The period of oscillation and the logarithmic decrement in vacuo of a new quartz wire employed for the present measurements are listed in Table 1.

The density of R22 was calculated from the Benedict-Webb-Rubin equation of state\(^14\). The calculated density values were of sufficient accuracy to evaluate gas viscosities\(^7\).

R22 (purity: above 99%\(^\circ\)) was supplied by the...