Prediction of the Latent Heat of Vaporization at Normal Boiling Point by use of Refractive Index

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The latent heat of vaporization at normal boiling point of 479 compounds (373 hydrocarbons and 106 non-hydrocarbons) was predicted successfully by use of refractive index. The refractive indices of 601 compounds (377 hydrocarbons and 224 non-hydrocarbons) at 20°C could satisfactorily be predicted within the maximum error of 2.7% by the newly-proposed group contribution method.

The maximum errors resulted from the prediction of latent heat of vaporization at normal boiling point by use of experimental refractive index and predicted refractive index were 6.5% and 11.3%, respectively.

1. Introduction

The latent heat of vaporization is one of the most fundamental and important factors for designing many thermal equipment and facilities. Especially, the latent heat of vaporization at normal boiling point is required and useful for calculations of critical properties⁶⁾, vapor pressure⁷⁾ and latent heat of vaporization of a compound at other temperatures⁸⁾.

A considerable number of techniques for prediction of the latent heat of vaporization at normal boiling point exist in the literature. These methods usually require critical temperature and critical pressure^{3),9)} and parachor and polarity number¹⁾. In our previous work, the group contribution method was proposed for aliphatic hydrocarbons⁴⁾.

By using the method presented in this paper, the latent heat of vaporization can be predicted from the refractive index and the normal boiling point, which can be obtained rather readily. As one of the predictive methods for refractive index, the group contribution method was proposed for aliphatic hydrocarbons at 25°C in our previous paper⁵⁾. This method is very simple and requires only a chemical formula of the molecule and its molecular weight. In this paper, the newly developed group contribution method for refractive index at 20°C is described and the calculation of the latent heat of vaporization at normal boiling point based on the refractive index is also described.

2. A Method for Prediction of the Latent Heat of Vaporization at Normal Boiling Point

Many methods have been proposed by earlier workers for predicting the latent heat of vaporization at normal boiling point. However, no method coupled with refractive index is yet available in the literature.

It was found that the latent heat of vaporization at normal boiling point (ΔH_{vb}) could be related to the refractive index as follows:

$$\Delta H_{vb} = \alpha ({}^nD^{20}) T_b \quad (1)$$

where

α : parameter [cal/g·mol·K]

${}^nD^{20}$: refractive index at 20°C by
Sodium D-line [—]

T_b : normal boiling point [K]

α in Eq. (1) is a parameter which is newly defined and is determined by use of experimental data.

The refractive index is one of the most fundamental properties, as is the normal boiling point. A large number of experimental data are available in many kinds of handbooks and data books. However, if no experimental refractive index data are available, the group contribution method, which needs no physical properties, is convenient and useful for predicting refractive index. The newly extended and useful group contribution method for predicting refractive index will be presented later. Also if no normal boiling point data are available, values of normal boiling point can be predicted accurately by those methods available in the literature⁸⁾.

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3. Prediction of Refractive Index by the Group Contribution Method

In this paper, the group contribution method has been developed to predict refractive indices of liquids. The method is commonly recognized as one of the reasonable methods to predict the physical properties of a fluid when no data are available. In our previous works, the following physical properties of aliphatic hydrocarbons, for instance, the liquid molar volume at 25°C⁴⁾, the latent heat of vaporization at normal boiling point⁴⁾ and the refractive index at 25°C⁵⁾, were successfully predicted by the group contribution method that requires only the knowledge of the molecular formula of the substance. This could be the greatest advantage of the method.

The refractive index at 20°C is calculated from the following group contribution method:

$$n_D^{20} = M / \sum \Delta d_i \quad (2)$$

where, n_D^{20} is the refractive index at 20°C by sodium D-line, M is the molecular weight and Δd_i is the group increment of i -th functional group for the refractive index at 20°C.

The method used for the determination of the group increment at 20°C is similar to that used at 25°C in our previous paper⁵⁾. The group increments determined for calculations of refractive indices at 20°C are shown in **Table 1**. There is no distinction for the isomers which made up from the same groups and the same group numbers. For calculation of such isomers, the results calculated by using the increments in **Table 1** give the same values of refractive indices. For example, 2,2-dimethylhexane and 3,3-dimethylhexane are made up of four $-\text{CH}_3$ groups, three $-\text{CH}_2-$ groups and one $-\text{C}-$ group, and the calculated refractive indices for those two substances are both 1.4044.

The experimental refractive index data, which were utilized for determination of the values of the individual group increments, were taken from the API data¹¹⁾, Lange's Handbook of Chemistry²⁾ and CRC Handbook of Chemistry and Physics¹²⁾.

An example of calculation of the refractive index at 20°C is shown in Appendix.

The presented method for prediction of the refractive index at 20°C was tested for 601 compounds (377 hydrocarbons and 224 non-hydrocarbons) and the results obtained were compared with those obtained experimentally^{2),11),12)}. It was

Table 1 The Group Increments for Calculations of the Refractive Indices at 20°C

Increments	Δd_i	Increments	Δd_i
Nonring increments		Nitrogen increments	
$-\text{CH}_3$	12.287	$-\text{NH}_2$	11.145
$-\text{CH}_2-$	9.525	$-\text{NH}-$	9.011
$-\text{CH}-$	6.668	$-\text{N}-$ (nonring)	6.790
$-\overset{ }{\underset{ }{\text{C}}}-$	3.610	$=\text{N}-$ (ring)	9.366
$=\text{CH}_2$	11.503	$-\text{CN}$	18.388
$=\text{CH}-$	8.471	$-\text{NO}_2$	31.374
$=\text{C}-$	5.327	Oxygen increments	
$=\text{C}=$	6.292	$-\text{OH}$ (alcohol)	12.182
$\equiv\text{CH}$	10.939	$-\text{OH}$ (phenol)	11.638
$\equiv\text{C}-$	7.175	$-\text{O}-$ (nonring)	11.053
Ring increments		$-\text{O}-$ (ring)	13.203
$-\text{CH}_2-$	9.897	$-\overset{ }{\underset{ }{\text{C}}}=\text{O}$	18.423
$-\text{CH}-$	7.443	$\text{HC}=\text{O}$ (aldehyde)	20.905
$-\overset{ }{\underset{ }{\text{C}}}-$	5.014	$-\text{COOH}$ (acid)	31.797
$=\text{CH}-$	8.672	$\text{HCOO}-$ (formate)	32.659
$=\text{C}-$	5.704	$-\text{COO}-$	29.796
Double bond number correction in ring		(ester : except formate)	
$\begin{cases} n \leq 4 \\ n \geq 5 \end{cases}$	$\begin{cases} 0.0 \\ -2.484 \end{cases}$	Sulfur increments	
Halogen increments		$-\text{SH}$	21.635
$-\text{F}$	17.180	$-\text{S}-$ (nonring)	18.890
$-\text{Cl}$	25.083	$-\text{S}-$ (ring)	19.729
$-\text{Br}$	52.895	$=\text{S}$	20.244
$-\text{I}$	79.515		

Table 2 A Summary of Errors in the Calculations of Refractive Indices at 20°C

Range of Errors $E^*(\%)$	No. of Comp. with this Range of n_D^{20} Estimation Error	Per Cent of Comp. Studied within this Range
$0.0 < E \leq 1.0$	539	89.5
$1.0 < E \leq 2.0$	53	8.8
$2.0 < E \leq 3.0$	9	1.5
(Total)	601	100.0
Average % Error**	0.4%	
Maximum % Error	2.7%	

$$* : E = \frac{|n_D^{20}_{\text{exp}} - n_D^{20}_{\text{cal}}|}{n_D^{20}_{\text{exp}}} \times 100 \quad * : AE = \frac{\sum E}{\sum N_{\text{comp}}}$$

found that 89.7% of the calculated refractive indices were within 1% of the refractive indices obtained experimentally, 8.8% were within 1 to 2% and only 1.5% deviated more than 2%. The relative average error and the maximum error for the 601 compounds were found to be 0.4% and 2.7% (for benzylbromide), respectively. A summary errors is shown in **Table 2**.

4. Calculated Results of the Latent Heat of Vaporization at Normal Boiling Point

The parameter α of Eq. (1) has been determined

from the experimental data: the refractive indices at 20°C^{(2), (11), (12)}, the normal boiling points and the latent heat of vaporization at normal boiling point^{(7), (10), (13)} of the various compounds concerned. The values of parameter α thus determined are shown in **Table 3** in which they range from the minimum 12.76 for aromatic iodines to the maximum 18.76 for alcohols. The values of the latent heat of vaporization at normal boiling point were calculated by use of the following two methods. One is to calculate the latent heat from the ex-

perimental refractive index data (Method I) and the other from the predicted refractive indices (Method II). Results of the latent heat of vaporization at normal boiling point for 479 compounds (373 hydrocarbons and 106 non-hydrocarbons) calculated are compared with those obtained experimentally, and the summary of the errors resulting from such comparison is presented in **Table 4**. Method I was found to be slightly more accurate than method II. By method I, 47.8% of the estimated values of the 479 compounds were within 1% of those obtained experimentally, 29.0% were within 1 to 2%, 14.6% were within 2 to 3%, 4.8% were within 3 to 4%, and 3.8% deviated more than 4%. Similarly, by method II, 45.6% of the estimated values were within 1% of the experimental values, 28.4% were within 1 to 2%, 16.5% were within 2 to 3%, 5.4% were within 3 to 4%, and 4.1% deviated more than 4%. The relative average error and the maximum error are 1.4% and 6.5% (for methylacetate and *n*-propyl-*iso*-butyrate) respectively, for method I, and 1.5% and 11.3% (for carbontetrachloride), respectively, for method II.

5. Conclusions

The latent heat of vaporization at normal boiling point can be predicted satisfactorily by the newly-presented Eq. (1). This equation consists of the refractive index at 20°C, the normal boiling point and the parameter α . Also, the newly developed and useful method based on the group contribution concept is presented for prediction of the refractive index at 20°C. The predicted refractive indices are in good agreement with those obtained experimentally.

Table 3 Determined Values of α

Compounds	α [cal/g·mol·K]
Hydrocarbons	
Alkanes, Alkenes, Alkadienes	14.56
Alkynes	15.21
Alkyl Cyclopentanes	14.28
Alkyl Cyclohexanes	14.08
Alkyl Benzenes	13.86
Alkyl Naphthalenes	13.45
Non-Hydrocarbons	
Acids (Saturated Aliphatic Monocarboxylic Acid)	16.64
Alcohols	18.69
Amines	
Aliphatic Amines	15.98
Aromatic Amines	14.27
Esters	15.56
Ethers	14.94
Ketones	15.10
Nitriles	15.02
Phenols	15.02
Halogen Compounds	
Aliphatic Fluorine Compounds	16.46
Aliphatic Chlorine Compounds	14.82
Aliphatic Bromine Compounds	14.10
Aliphatic Iodine Compounds	13.71
Aromatic Fluorine Compounds	14.34
Aromatic Chlorine Compounds	14.15
Aromatic Bromine Compounds	13.50
Aromatic Iodine Compounds	12.76
Sulfur Compounds	
Alkane Thiols, Thiaalkanes	14.43
Dithiaalkanes, Thiacycloalkanes, Thiophenes, Benzenethiols	14.01

Table 4 A Summary of Errors in the Calculation of the Latent Heat of Vaporization at Normal Boiling Point

Range of Errors E*(%)	No. of Comp. with this Range of ΔH_{vb} Estimation Error		Per Cent of Comp. Studied within this Range	
	Method I	Method II	Method I	Method II
0.0 < E ≤ 1.0	229	218	47.8	45.6
1.0 < E ≤ 2.0	139	136	29.0	28.4
2.0 < E ≤ 3.0	70	79	14.6	16.5
3.0 < E ≤ 4.0	23	26	4.8	5.4
4.0 < E ≤ 5.0	7	9	1.5	1.9
5.0 < E ≤ 6.0	8	4	1.7	0.8
6.0 < E ≤ 7.0	3	3	0.6	0.6
7.0 < E	0	4	0.0	0.8
(Total)	479	479	100.0	100.0
Average % Error**	1.4%	1.5%		
Maximum % Error	6.5%	11.3%		

$$* : E = \frac{|\Delta H_{vb, \text{exp}} - \Delta H_{vb, \text{cal}}|}{\Delta H_{vb, \text{exp}}} \times 100 \quad * : AE = \frac{\sum E}{\sum N_{\text{comp}}}$$

For the 479 compounds studied the relative average error and the maximum error resulted from prediction of the latent heat of vaporization at normal boiling point by using the refractive index data obtained experimentally were 1.4% and 6.5%, respectively. However, by using Eq. (2), the corresponding errors resulted from prediction

of the latent heat of vaporization by use of the refractive index were 1.5% and 11.3%, respectively.

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Appendix

The use of **Table 1** is shown by calculating the refractive index of 1-methylnaphthalene at 20°C as follows:

exp. n_D^{20} 1.61755¹¹⁾

M : 142.190

$$\Delta d_i = \underbrace{\sum(-CH_3)}_{\text{non-ring increment}} + \underbrace{\sum(=CH-)}_{\text{ring increment}} + \underbrace{\sum(=C-)}_{\text{ring increment}} + (\text{double bond number correction in ring})$$

$$= (12.287) + (8.672 \times 7) + (5.704 \times 3) + (-2.484) = 87.619$$

$$n_D^{20} = 142.190 / 87.619 = 1.62282$$

$$\text{error} : \frac{|1.61755 - 1.62282|}{1.61755} \times 100 = 0.3(\%)$$

Nomenclature

AE=average error	[%]
n_D^{20} =refractive index at 20°C by Sodium D-line	[-]
Δd_i =group increment of <i>i</i> -th functional groups for the refractive index at 20°C	[-]
E=error	[%]
ΔH_{vb} =latent heat of vaporization at normal boiling point	[cal/g-mol]
M=molecular weight	[-]
N_{comp} =number of compounds	[-]
T_b =normal boiling point	[K]
α =parameter	[cal/g-mol·K]

Subscripts

cal=calculated
exp=experimental

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要 旨

屈折率を用いた標準沸点における蒸発潜熱の推算

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蒸発潜熱は、熱を伴う多くの機器の設計における、最も基礎的かつ重要な物性値の一つである。特に、標準沸点下の蒸発潜熱は、臨界特性⁶⁾、蒸気圧の計算⁷⁾、さらに任意の温度の蒸発潜熱の計算⁸⁾において基準値として用いられる等、その利用度は高い。

標準沸点における蒸発潜熱の推算方法としては、臨界温度および臨界圧力^{8),9)}あるいはパラコールおよび極性数¹⁾を用いる方法、そして筆者らの脂肪族炭化水素に対する原子団寄与の方法⁴⁾がある。

本研究において提案した方法は、いままでにその報告例のほとんどない屈折率を用いるものである。屈折率に対しては、新たに提案した **Table 1** を用いる原子団寄与による推算方法を

示した。その精度は、601 の物質 (377 の炭化水素および 224 の非炭化水素) に対して **Table 2** に示されたごとく平均誤差は 0.4% で最大誤差は、臭化ベンゼンに対する 2.7% であった。

本研究で提案したパラメーター α を実測データを用いて決定し、その値を **Table 3** に示した。標準沸点における蒸発潜熱を、実測値の 20°C の屈折率を用いる方法 (Method I) および原子団寄与の方法で推算した屈折率を用いる方法 (Method II) により計算し、その結果の概略を **Table 4** に示した。その精度は、479 の物質 (373 の炭化水素および 106 の非炭化水素) に対して、Method I および Method II の平均誤差は 1.4% および 1.5% であり、最大誤差はそれぞれメチルアセテートと *n*-プロピル-イソ-ブチレートに対する 6.5%、および四塩化炭素に対する 11.3% であった。

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Keywords

Latent heat, Vaporization, Refractive index, Group contribution method, Hydrocarbon