An Empirical Method for Estimating Normal Boiling Point and other Physical Properties of Alkene Hydrocarbons

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The structural variation in the physical properties of alkene hydrocarbons is determined by the number and relative position of double bonds and side chains in the molecule. Owing to the presence and mutual influence of two different kinds of chemical bonds and side chains, correlation between properties and molecular structure is far more complicated than that in the case of isoparaffins, for which an elaborate set of structural parameters can be successfully used[1,2]. Although a few attempts were made to correlate the boiling point[3,4] or critical constants[5,6] with the molecular structure of alkenes, no extensive method has been established at the present stage.

In this paper, an empirical relation between the physical properties of linear and branched alkenes and their molecular structure is proposed. The "effective carbon number" method which has been used for isoparaffins in the previous report[2] is again adopted. As will be shown later, a characteristic constant called "effective carbon number" can be defined for all the alkene hydrocarbons. Thus, this effective carbon number is first calculated by the proposed equation and then, by the use of a previously presented nomogram[2], the normal boiling point and other physical properties of the alkenes can be estimated from the knowledge of the structural formula alone.

Effective Carbon Number

When the boiling points of normal paraffins are plotted against the number of carbon atoms, a family of curves for different pressures is obtained. Then, reading the boiling points of a given alkene on these curves, one can obtain a set of values of an "effective number" of carbon atoms, each corresponding to every different pressure. These sets of values for several alkenes obtained by this procedure are listed in Table I together with the used values of the boiling point[7,8], where a reasonable constancy of the values is observed over a considerably wide range of pressure. This effective number of carbon atoms depending on the structural feature of each compound but not on the external condition is called the "effective carbon number" and hereafter denoted by n^*. It is shown that the proper assignment of the n^* value is advantageous not only for the estimation of the boiling point of the alkenes at various external pressures but also for that of other physical properties such as the critical constants, as in the case of isoparaffins[2].

TABLE I. CONSTANCY OF EFFECTIVE CARBON NUMBER OF ALKENES AT VARIOUS EXTERNAL PRESSURES

Compound	Pressure, mmHg	10	20	60	200	400	760
1-Butene	T_b[7] (°C)	−81.5	−72.89	−57.15	−36.10	−21.62	−6.26
	n^*	3.88	3.87	3.86	3.86	3.86	3.85
2-Methylpropene	T_b[7] (°C)	−81.95	−73.37	−57.664	−36.666	−22.227	−6.900
	n^*	3.87	3.85	3.84	3.85	3.84	3.84
1,3-Butadiene	T_b[8] (°C)	−79.7	−71.0	−55.1	−33.9	−19.3	−4.5
	n^*	3.92	3.93	3.93	3.90	3.89	3.86

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Structural Units

The molecular structure of alkenes can be specified by the number and the relative position of double bonds and those of branching units. Therefore, if the mutual influence among these units is properly estimated, the deviation of the effective carbon number from the real one may be expressed as a linear combination of several factors, each corresponding to a double bond or a branching unit. Although various kinds of methods for such factorization would be possible, only the linear factorization is used here because of its simplicity for practical purposes.

The following four groups of carbon atoms are adopted as the structural units of alkenes: i. e. (I) double bond existing in the linear portion of the molecule, (II) double bond attached to branching atoms, (III) trifunctional branching and (IV) tetrafunctional branching. Schematically, these are

(I) -C=C-, (II) -C=C(-C)- or -C-C(-C)=C(-C)-,

(III) -C(-C)-C- and (IV) -C(-C)(-C)-C-

For each of the four structural units, the following equation is obtained after some troublesome analysis of available boiling point data:

$$\Delta n_{\mathrm{I}} = 0.24 - 0.12b_1 + 0.05b_2 \quad (1)$$

$$\Delta n_{\mathrm{II}} = 0.24 - 0.08b_1 + 0.07b_2 \quad (2)$$

$$\Delta n_{\mathrm{III}} = 0.28 - 0.06c_2 + 0.06c_3 \quad (3)$$

$$\Delta n_{\mathrm{IV}} = 0.73 - 0.14c_2 + 0.05c_3 \quad (4)$$

The difference of the effective carbon number n^* from the real carbon number n is then given by the sum of these contributions,

$$\Delta n = n - n^* = \sum_{\mathrm{I}} \Delta n_{\mathrm{I}} + \sum_{\mathrm{II}} \Delta n_{\mathrm{II}} + \sum_{\mathrm{III}} \Delta n_{\mathrm{III}} + \sum_{\mathrm{IV}} \Delta n_{\mathrm{IV}} \quad (5)$$

where the summation extends over all structural units of each type. The four parameters, b_1, b_2, c_2 and c_3, in Eqs. 1 to 4 are defined as follows:

- b_1—the number of carbon-carbon bonds adjacent to the double bond.
- b_2—the number of carbon-carbon bonds (single and double) next but one to the double bond.
- c_2—the number of the second neighbor carbon atoms of the branching point (tertiary or quaternary carbon atom).
- c_3—the number of the third neighbor carbon atoms of the branching point (tertiary or quaternary carbon atom).

As is easily seen, the intrinsic contribution of the structural unit I, III and IV is represented by the first term of Eqs. 1, 3 and 4, respectively, while two other terms which represent the contribution of adjacent carbon atoms to each structural unit are introduced to take the mutual correlation of the structural units into account. The choice of type II as an independent structural unit is also due to the fact that the correlation of the double bond with the branching is so strong that it can not be treated separately.

It is obvious from the definition that the effective carbon number of isoparaffins is given by

$$n^* = n - \sum_{\mathrm{III}} (0.28 - 0.06c_2 + 0.06c_3) - \sum_{\mathrm{IV}} (0.73 - 0.14c_2 + 0.05c_3) \quad (6)$$

The accuracy of this equation is of the same degree as that of Eq. 41 in the previous paper[2], which is expressed in terms of the Wiener parameters[1].

Example of Calculation

The present method consists of the following two procedures:

(1) Effective carbon number n^* is calculated by Eq. 5. Only the structural formula of alkene in question is required.

(2) The vapor pressure-temperature relationship, the critical constants and the heat of vaporization at normal boiling point can be read on nomogram[2] by using the value of n^* just obtained.

For clear understanding of the method, calculation of the normal boiling point of 3, 5, 5-trimethyl-1-hexene is presented as an example.

3, 5, 5-Trimethyl-1-hexene

$C^1=C^2-C^3(-C^7)-C^4-C^5(-C^8)(-C^9)-C^6$

This compound contains the aforementioned structural units of I, III and IV types. The unit of type I is attached to one carbon-carbon bond to be counted as b_1, say C^2–C^3, and to two bonds to be counted as b_2, say C^3–C^4 and C^3–C^7; hence

$$\Delta n_{\mathrm{I}} = 0.24 - 0.12 \times 1 + 0.05 \times 2 = 0.22$$

The structural unit of type III or tertiary carbon atom C^3 has two second neighbors, say C^1 and C^5, and three third neighbors, say C^6, C^8 and C^9, hence

$$\Delta n_{\mathrm{III}} = 0.28 - 0.06 \times 2 + 0.06 \times 3 = 0.34$$

Quaternary carbon atom C^5 has one second neighbor, C^3, and two third neighbors, C^2 and C^7, and so

$$\Delta n_{\mathrm{IV}} = 0.73 - 0.14 \times 1 + 0.05 \times 2 = 0.69$$

TABLE II. NORMAL BOILING POINT OF MONOALKENES

Compound	Normal boiling point T^0_b, °C		Effective carbon number, n^*	
	Obs.[9]	Calcd.	Obs.	Calcd.
Ethylene	−103.7	−104.0	1.76	1.76
Propylene	−47.7	−47.0	2.86	2.88
1-Butene	−6.3	−6.0	3.85	3.83
2-Butene	1.	2.0	4.04	4.00
2-Methylpropene	−6.9	−2.0	3.84	3.92
1-Pentene	29.9	30.0	4.83	4.83
2-Pentene	36.1	34.0	5.00	4.95
2-Methyl-2-butene	38.6	36.0	5.07	5.00
2-Methyl-1-butene	31.2	31.0	4.86	4.85
3-Methyl-1-butene	20.1	20.0	4.55	4.56
1-Hexene	63.5	63.0	5.83	5.83
2-Hexene	68.2	67.0	5.98	5.95
3-Hexene(*trans*)	67.1	65.0	5.93	5.90
2-Methyl-1-pentene	62.2	63.0	5.80	5.85
3-Methyl-1-pentene	54.2	56.0	5.54	5.62
4-Methyl-1-pentene	53.9	54.0	5.53	5.55
2-Methyl-2-pentene	65.0	66.0	5.88	5.93
3-Methyl-2-pentene	68.0	66.0	5.97	5.93
4-Methyl-2-pentene	57.0	56.0	5.60	5.62
2-Ethyl-1-butene	64.7	62.0	5.76	5.78
2,3-Dimethyl-1-butene	55.6	51.0	5.58	5.46
3,3-Dimethyl-1-butene	41.2	41.0	5.14	5.14
2,3-Dimethyl-2-butene	73.	71.0	6.1	6.08
1-Heptene	93.6	93.0	6.83	6.83
2-Heptene	98.5	97.0	7.00	6.95
3-Heptene	95.6	95.0	6.90	6.90
2,3,3-Trimethyl-1-butene	77.9	77.0	6.30	6.26
1-Octene	121.3	120.0	7.83	7.83
2-Isopropyl-3-methyl-1-butene	113.6	100.0	7.55	7.08
1-Nonene	146.9	147.0	8.84	8.83
2,3,3,4-Tetramethyl-1-pentene	133.2	133.0	8.30	8.32
1-Decene	170.6	170.0	9.84	9.83
2,3,3,4,4-Pentamethyl-1-pentene	158.8	157.0	9.33	9.27

n^*_{obs}=Effective carbon number at normal boiling point (cf. Table I)
n^*_{calcd}=Calculated value by Eq. 5

Thus, the summing up of the above three Δn_j's gives,

$$\Delta n = 0.22 + 0.34 + 0.69 = 1.25$$

$$\text{or} \quad n^* = 9 - 1.25 = 7.75$$

Then, using the nomogram[2], 118°C is obtained for the normal boiling point which is to be compared with the observed value 119.4°C[9].

Comparison with Experimental Data

A test of the present method by the procedure described in the last section was carried out for 188 monoalkenes and 46 dialkenes.

The average deviation of the calculated values of normal boiling point of the monoalkenes from the literature values[9,10] was as small as 2.5°C, with the maximum deviation −17°C for 2-*tert*-butyl-3,3-dimethyl-1-butene. Only ten percent of the tested compounds showed an error higher than 5°C. Table II shows about 30 examples of this test.

In the case of dialkenes with no "conjugated double bond", the average deviation of the normal boiling point was found to be about 2.4°C, the maximum deviation was −11°C for 1,4-heptadiene, and the deviation was less than 5°C for 87 percent of the tested compounds. Table III shows the results for typical examples.

In the presence of the conjugated double

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TABLE III. NORMAL BOILING POINT OF DIALKENES

Compound	Normal boiling point T^0_b, °C		Effective carbon number, n^*	
	Obs.[10]	Calcd.	Obs.	Calcd.
1,4-Hexadiene	65.	61.0	5.88	5.78
1,5-Hexadiene	59.5	58.0	5.70	5.66
2-Methyl-1,4-pentadiene	56.	59.0	5.60	5.70
3-Methyl-1,4-pentadiene	55.	49.0	5.57	5.40
1,4-Heptadiene	100.8	90.0	7.10	6.73
1,5-Heptadiene	94.3	91.0	6.85	6.78
2-Methyl-1,5-hexadiene	92.1	89.0	6.78	6.68
3-Methyl-1,5-hexadiene	80.5	82.0	6.39	6.46
5-Methyl-1,4-hexadiene	91.8	91.0	6.77	6.76
2,4-Dimethyl-1,4-pentadiene	81.3	89.0	6.41	6.70
1,7-Octadiene	117.5	116.0	7.69	7.66
3-Methyl-1,5-heptadiene	110.5	112.0	7.44	7.51
2-Methyl-1,6-heptadiene	115.6	116.0	7.65	7.68
2,4-Dimethyl-1,5-heptadiene	132.1	134.0	8.29	8.41
2,6-Dimethyl-2,6-octadiene	166.9	169.0	9.67	9.86

n^*_{obs}=Effective carbon number at normal boiling point (cf. Table I)
n^*_{calcd}=Calculated value by Eq. 5

TABLE IV. COMPARISON OF CALCULATED CRITICAL CONSTANTS AND HEAT OF VAPORIZATION WITH LITERATURE VALUES

Compound	Effective carbon number, n^*	Critical temperature °K			Critical pressure atm.			Heat of vaporization (kcal./mol.) at T^0_b		at 25°C	
	Calcd.	Obs.[7]	Calcd.	Thodos[5]	Obs.[7]	Calcd.	Thodos[5]	Obs.[7]	Calcd.	Obs.[7]	Calcd.
Ethylene	1.76	282.4	—	290.3	50.0	—	50.7	3.24	—	—	—
Propylene	2.88	365.0	363.0	367.3	45.6	43.0	45.7	4.40	4.36	—	3.27
1-Butene	3.83	419.6	415.0	425.3	39.7	37.0	39.8	5.24	5.14	4.87	4.70
2-Butene (*cis*)	4.00	430.2	424.0	429.3	41.	38.0	37.4	5.58	5.27	5.30	4.95
(*trans*)				426.3			37.3	5.44		5.15	
2-Methylpropene	3.92	417.9	422.0	425.2	39.5	36.0	40.4	5.29	5.22	4.92	4.84
1-Pentene	4.83	474.2	461.0	471.4	40.	34.0	35.2	—	5.95	—	6.02
2-Pentene	4.95	475.6	466.0	471.5	40.4	34.0	32.9	—	6.05	—	6.19
2-Methyl-2-butene	5.00	470.2	468.0	471.2	34.	33.0	33.2	—	6.09	—	6.06
2-Methyl-1-butene	4.85	—	462.0	471.6	—	34.0	35.6	—	5.97	—	6.25
3-Methyl-1-butene	4.56	464.8	450.0	—	33.9	35.0	—	—	5.75	—	5.69

bond, Eq. 5 fails to express the difference of the effective carbon number of compounds from the real carbon number. However, the effective carbon number itself can also be defined for this type of compound (see Table I), and a conventional procedure is possible. That is, if one boiling point datum is available, n^* can be obtained on nomogram without the aid of Eq. 5.

Table IV shows the comparison of the estimated values of critical temperature, critical pressure and heat of vaporization with the observed values[7], where the critical constants estimated by the Thodos' method[5,6] are also given for comparison.

The application of Eq. 6 to isoparaffins is also satisfactory, though the results are not given here*3. It is especially favorable for the estimation of the heat of vaporization at normal boiling point and the critical temperature.

Summary

A method of estimating the structural variation in the boiling point and other physical properties of alkenes is developed. By this method, all properties are expressed in terms of a structural constant called the "effective carbon number" which depends on the number and relative position of double bonds and those of side chains but not on external variables such as the temperature. An empirical equation is presented to correlate the effective carbon number with molecular structure. By combining the use with the previously presented nomogram*4, it is proved to be quite

*3 Details of the results will be published elsewhere.

*4 Copies of original drawing of the nomogram will be sent upon request.

useful for rapid evaluation of various properties including the temperature-vapor pressure relationship and the critical constants.

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