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General Equation for Expressing the Physicochemical Properties of Aliphatic Alcohols

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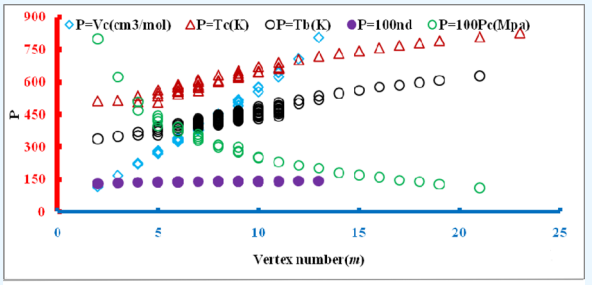
ABSTRACT: In this work, two general equations were proposed to express the nonlinear and linear changes in physicochemical properties of aliphatic alcohols, involving boiling point, refractive index, critical temperature, critical volume, and so on. The two general equations all are expressed with the same six molecular descriptors. The results show that the linear and nonlinear change properties of aliphatic alcohols have good correlations with the same six molecular descriptors. Using the obtained correlation equations, various properties of aliphatic alcohols without experimental values were predicted, involving 15 normal boiling points, 96 refractive indexes, 105 critical temperatures, 109 critical pressures, 100 liquid densities, 136 heat capacities, 107 critical volumes, and 130 enthalpies of the formation of liquid, a total of 798 values. The relationship between the nonlinear and linear change properties can be deduced by using the obtained general equations, which connect different properties of aliphatic alcohols. In addition, this paper combined the general estimation models used in the properties of aliphatic alcohols and aliphatic primary amines, and then, by taking the boiling point and critical temperature as examples, a general estimation model with good correlation and high prediction accuracy was obtained via adding another two molecular structure characteristic parameters. It is a meaningful exploration for establishing general models for monosubstituted alkane RX compounds with different substituents in the future.



The properties (P) of aliphatic alcohols can be expressed as:

$$P = f(m, S_{VNE}, \Delta(AOEI), \Delta(AIMPI), \Delta(APEI), G_N)$$

1. INTRODUCTION

Aliphatic alcohols are a kind of raw material used widely and have a great demand in manufacturing and chemical production. However, their experimental data of physicochemical properties are lacking, which are indispensable in scientific research and industrial production. The CRC Handbook of Chemistry and Physics,[1] an important source of data on physicochemical properties, involves only 54 records of boiling point and 23 records of heat capacities of aliphatic alcohols. Therefore, it is necessary and meaningful to estimate the physicochemical properties of aliphatic alcohols. Kontogeorgis[2] pointed out that enterprises wish to have a general model of the thermodynamic and transport properties of organics applied to industrial production, but this may be utopian. As known, quantitative structure−property relationship (QSPR) is one of the significant methods to understand and predict the properties of compounds and is widely used in environmental testing, medicine, and other fields. The QSPR method combines mathematical statistical methods with chemical theoretical calculation methods to quantitatively describe the relationship between the structure and properties of organic compounds.[3−7] Generally, QSPR methods consist of three main parts:[5] (i) calculation of molecular descriptors and collection of experimental data; (ii) development of QSPR models and validation; and (iii) prediction and interpretation. Using QSPR methods, the relationship between the physicochemical properties of compounds and the molecular structure can be expressed by a series of molecular descriptors. It has the following general form

$$\text{Property} = f(\text{descriptors}) \quad (1)$$

In this work, we try to use the QSPR method and calculate molecular descriptors to express the relationship between the molecular features and various physicochemical properties of aliphatic alcohols and to predict the properties of aliphatic alcohols without experimental values. Furthermore, we try to explore the general estimation models for the properties of both aliphatic primary amines and aliphatic alcohols.

In 2022, Cao et al. proposed a general equation for the boiling point of aliphatic alcohols by the QSPR method,[8] as shown in eq 2, where n represents the number of carbon atom and SCNE and ΔPEI are the sum of carbon number effect and polarization effect index difference, respectively.

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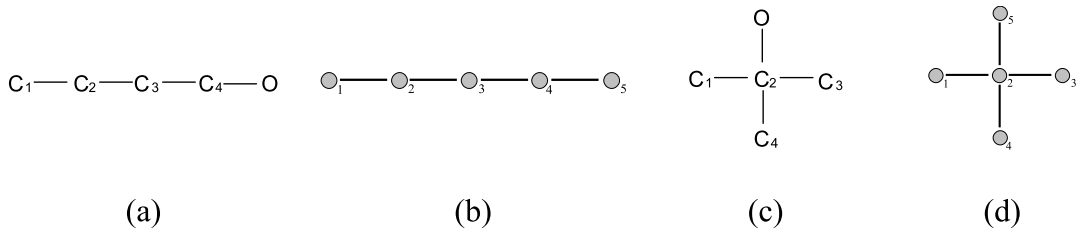

Figure 1. Molecular skeleton diagram (a,c) and molecular graph (b,d) for C_4H_9OH isomers.

$$\ln(\mathrm{Tb}) = 5.7785 + 0.031339(\mathrm{n} - 1) + 0.051561(S_{\mathrm{CNE}}) - 1.74757(\Delta\mathrm{PEI}/\mathrm{n}) \quad (2)$$

The molecular structures of alcohols are different from that of alkanes, and there is a polar functional hydroxyl (OH) in aliphatic alcohol ROH. Therefore, the boiling points of alcohols are affected by the number of carbon atoms, the carbon skeleton, and the position of OH attached to the alkyl chain. The influence of the latter two factors on the boiling point can be expressed by $\Delta PEI/n$ and the PEI of an alcohol, which are related to the position of the alkyl skeleton and OH in the molecule. For an alcohol molecule with n carbon atoms, ΔPEI = PEI(branched alcohol) − PEI(linear chain alcohol). The parameters proposed in eq 2 are easy to calculate. In Cao's report,[8] the average absolute error (AAE) between the experimental value and the calculated value is 4.40 K, and the average absolute percentage error (AAPE) is 1.01%, which can be used to predict the boiling point of aliphatic alcohols without experimental values.

Whether eq 2 can be used as a model equation for expressing other property changes of aliphatic alcohols is a topic worth studying. Therefore, we attempt to establish the relationship between the molecular structure and properties of aliphatic alcohols and obtain a general estimation model with higher accuracy via selecting and calculating molecular descriptors.

2. RESULTS AND DISCUSSION

The nomenclature used in this article is shown in the appendix.

2.1. Theoretical Analysis of Factors Affecting the Property of Aliphatic Alcohols. Recently, Cao et al. proposed an equation for estimating physicochemical properties of noncyclic alkanes,[9] named the "NAPA equation", as shown in eq 3, where the molecular descriptors involve carbon atom number *n*, sum of carbon number effects SCNEs, average odd−even index difference Δ(AOEI), and average intramolecular polarization index difference Δ(AIMPI).

$$\ln(P_{(n)}) = a + b(n - 1) + cS_{\mathrm{CNE}} + d(\Delta(\mathrm{AOEI})) + f(\Delta(\mathrm{AIMPI})) \quad (3)$$

In eq 3, the *a*, *b*, *c*, *d*, and *f* are coefficients and are obtained by regression analysis.

The molecular skeleton of alkanes has only carbon atoms and no other functional groups, while the aliphatic alcohols have a polar OH. In the molecular skeleton diagram, we think that the position of OH will affect the molecular skeleton, so the vertex number *m* (a total of carbon and oxygen atoms) replaces the carbon atom number n as one of the molecular descriptors, and the calculation of SCNE should also be based on the vertex number. That is, the SCNE should be changed into SVNE (the "sum of carbon number effect" is changed into "sum of vertex number effect"). Then, the polarization effect between OH and the carbon skeleton should be characterized by the average polarization effect index Δ(APEI). The influence of OH on the carbon skeleton can be characterized by group influence factor GN, namely, the ratio of group number to the number of carbon atoms. Thus, a general equation for estimating the physicochemical properties of aliphatic alcohols can be proposed.

2.1.1. Calculation of Molecular Descriptors of Aliphatic Alcohols. In aliphatic alcohols, there are generally three factors affecting their physicochemical properties: the number of vertex, the molecular skeleton, and the polar hydroxyl. Thus, the calculation of molecular descriptors mainly includes the parameters related to the number of vertex (the vertex number m and the "sum of vertex number effects", SVNEs), the parameters related to the molecular skeleton [average odd−even index difference Δ(AOEI) and average intramolecular polarizability index difference Δ(AIMPI)], and the influential parameters of OH on the carbon skeleton [average polarizability effect index Δ(APEI) and hydroxyl group influence factor GN].

2.1.2. Calculation of Parameters Related to the Number of Vertex. The general formula of aliphatic alcohols is $C_nH_{2n+1}OH$. According to the report by Cao et al.,[8] here, the number of vertex m and the SVNE involving the O atom are employed to express the effect of vertex numbers on the property of aliphatic alcohols. Therefore, the SVNE is calculated with the term of $\sum_{i=2}^{m}\left(\frac{1}{i-1}\right)$ in this work.

2.1.3. Calculation of Parameters Related to the Molecular Skeleton. Aliphatic alcohol isomers containing the same number of carbon atoms may have different molecular skeletons; therefore, the changes in the physicochemical properties of isomers are related to the differences between the skeleton of branched aliphatic alcohols and linear aliphatic alcohols. In this article, the average odd−even index difference Δ(AOEI) and the average intramolecular polarizability index difference Δ(AIMPI) are used to represent the molecular skeleton differences between branched and linear aliphatic alcohols.

2.1.3.1. Average Odd−Even Index Difference. OEI is a topological index that can be used to characterize the skeleton of molecules,[10] which can be calculated by eq 4. Where *m* is the number of vertex in the molecular graph and *S* is a derivative matrix which is from the distance matrix *D*, where $S_{ij} = (D_{ij}) - 2$ (when $i = j$, let $S_{ij} = 0$).

$$\mathrm{OEI} = \sum_{i=1}^{m}\sum_{j\neq i}^{m}[(-1)^{D_{ij}-1}S] \quad (4)$$

Taking butanol (C_4H_9OH) as an example, parts (a) and (c) in Figure 1 represent the molecular skeletons of the two isomers of C_4H_9OH, respectively. The (b) and (d) represent

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their corresponding molecular graphs. Since the position of the OH affects the molecular skeleton, so atoms other than hydrogen atoms are defined as vertices. In (a) and (c), the number indicates the number of carbon atom, in (b) and (d), the number represents the number of vertex, where (a) and (b) represent 1-butanol and (c) and (d) represent 2-methyl-2-propanol.

A matrix describing the molecular skeleton was constructed from the molecular graph, as shown in Figure 2. The distance matrix D(b) and D(d) in Figure 2 correspond to the molecular graphs (b) and (d) in Figure 1, and D_{ij} represents the distance between the vertex i and vertex j.

$$\mathrm{D(b)}=\begin{bmatrix}0&1&2&3&4\\1&0&1&2&3\\2&1&0&1&2\\3&2&1&0&1\\4&3&2&1&0\end{bmatrix} \qquad \mathrm{D(d)}=\begin{bmatrix}0&1&2&2&2\\1&0&1&1&1\\2&1&0&2&2\\2&1&2&0&2\\2&1&2&2&0\end{bmatrix}$$

Figure 2. Distance matrix of C_4H_9OH isomers [Figure 1(b,d)] corresponding to the molecular graph.

The OEI value can be obtained by using the distance matrix D and derivative matrix S. The OEI values of molecular graphs (b) and (d) in Figure 1 are OEI(b) = 6.8194 and OEI(d) = 5.0000, indicating that (a) and (c) in Figure 1 have OEI values of 6.8194 and 5.0000, respectively.

In this paper, we intend to propose a general estimation model based on the properties of aliphatic alcohols in linear skeletons; therefore, the difference value (Δ) is used to represent the effect of structural or polar changes on aliphatic alcohols. Therefore, the ΔOEI[11] is divided by the number of vertex to avoid the topological index being affected by the number of vertex, as shown in eq 5, where "bran" represents the branched aliphatic alcohol, "lin" represents the linear aliphatic alcohol, m represents the number of vertex, and the difference value of the linear aliphatic alcohol is zero.

$$\Delta(\mathrm{AOEI}) = \Delta\mathrm{OEI}/m = [(\mathrm{OEI})_{\mathrm{bran}} - (\mathrm{OEI})_{\mathrm{lin}}]/m \quad (5)$$

2.1.3.2. Average Intramolecular Polarization Effect Index Difference. According to Cao's report,[12] the IMPI can be calculated from eq 6. Here, we use IMPI to distinguish the molecular structures of aliphatic alcohols. That is, we first take the OH group as a CH3 group and then calculate the IMPI of ROH (i.e., ROH is converted into RCH_3).

$$\mathrm{IMPI} = \Sigma\mathrm{PEI}(i) \quad (6)$$

In which, the PEI(i) is the sum of the polarization effect indices of the groups attached to the i-th vertex atom, the i-th vertex atom in the aliphatic alcohol molecule is regarded as the starting atom, and the other part is considered as the alkyl group. The PEI(i) value of alkyl group R_i can be calculated via employing the ΔPEI values of carbon atoms in R_i (see Table 1), that is, PEI(i) = ΣΔPEI(i). Take Figure 1 (b) for example, the vertex 1 connects with a butyl, the vertex 2 connects with a methyl and a propyl, and the vertex 3 connects with two ethyl.

The calculations of IMPI of Figure 1b,d, for examples, are described as follows.

IMPI(b)

vertex 1: PEI(1) = 1.00000 + 0.14053 + 0.04813 + 0.02350 = 1.21216

vertex 2: PEI(2) = 2 × 1.00000 + 0.14053 + 0.04813 = 2.18866

vertex 3: PEI(3) = 2 × 1.00000 + 2 × 0.14053 = 2.28106

vertex 4: PEI(4) = 2 × 1.00000 + 0.14053 + 0.04813 = 2.18866

vertex 5: PEI(5) = 1.00000 + 0.14053 + 0.04813 + 0.02350 = 1.21216.

IMPI(b) = ΣPEI(i) = 1.21216 + 2.18866 + 2.28106 + 2.18866 + 1.21216 = 9.0827.

IMPI(d)

vertex 1: PEI(1) = 1.00000 + 3 × 0.14053 = 1.42159

vertex 2: PEI(2) = 4 × 1.00000 = 4.00000

vertex 3: PEI(3) = 1.00000 + 3 × 0.14053 = 1.42159

vertex 4: *PEI*(4) = 1.00000 + 3 × 0.14053 = 1.42159

vertex 5: *PEI*(5) = 1.00000 + 3 × 0.14053 = 1.42159.

IMPI(d) = ΣPEI(i) = 1.42159 + 4.00000 + 1.42159 + 1.42159 + 1.42159 = 9.6863.

Similarly, the topological index of each structure should be based on linear aliphatic alcohols, from which Δ(AIMPI) can be obtained, as shown in eq 7.

$$\Delta(\mathrm{AIMPI}) = \Delta(\mathrm{IMPI})/m = [(\mathrm{IMPI})_{\mathrm{bran}} - (\mathrm{IMPI})_{\mathrm{lin}}]/m \quad (7)$$

2.1.4. Calculation of the Influential Parameters of Hydroxyl on the Skeleton. 2.1.4.1. Average Polarization Effect Index. Aliphatic alcohols ROH have a polar OH, in which the OH polarizes the alkyl R, resulting in an intramolecular polarization effect.[13] Cao et al.[14,15] pointed out that the PEI of alkyl R is calculated by using PEI(R) = ΣΔPEI(i). Here, we reshowed the PEI of straight alkyl $H(CH_2)_n$—and PEI increment ΔPEI of i-th carbon atom, as shown in Table 1.

Table 1. PEI of Alkyl $H(CH_2)_n$—and PEI Increment (ΔPEI) of the i-th Carbon Atom[a]

n	PEI	ΔPEI	n	PEI	ΔPEI
1	1.0000	1.00000	6	1.2359	0.00905
2	1.1405	0.14053	7	1.2414	0.00639
3	1.1887	0.04813	8	1.2461	0.00475
4	1.2122	0.02350	9	1.2498	0.00367
5	1.2260	0.01380	10	1.2527	0.00014

[a]Data from ref 15.

Taking 2-methyl-1-propanol as an example to illustrate the calculation of the PEI value, the molecular structural formula is shown in Figure 3, where the number above/below the carbon

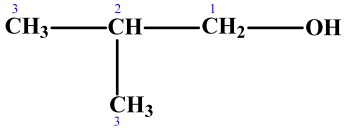

Figure 3. Molecular structural formula of 2-methyl-1-propanol.

atom represents the distance of the oxygen atom from the carbon atom (number of chemical bonds). The CH_2, CH, and CH_3 distance with OH are 1, 2, and 3 chemical bonds, respectively, and their ΔPEI(i) increments are 1.00000, 0.14053, and 0.04813 respectively. Thus, its PEI value is calculated as shown in eq 8.

$$\begin{aligned}\mathrm{PEI} &= \Delta\mathrm{PEI}(\mathrm{CH_2}) + \Delta\mathrm{PEI}(\mathrm{CH}) + 2\times\Delta\mathrm{PEI}(\mathrm{CH_3})\\ &= 1.00000 + 0.14053 + 2\times 0.04813\\ &= 1.2368\end{aligned} \quad (8)$$

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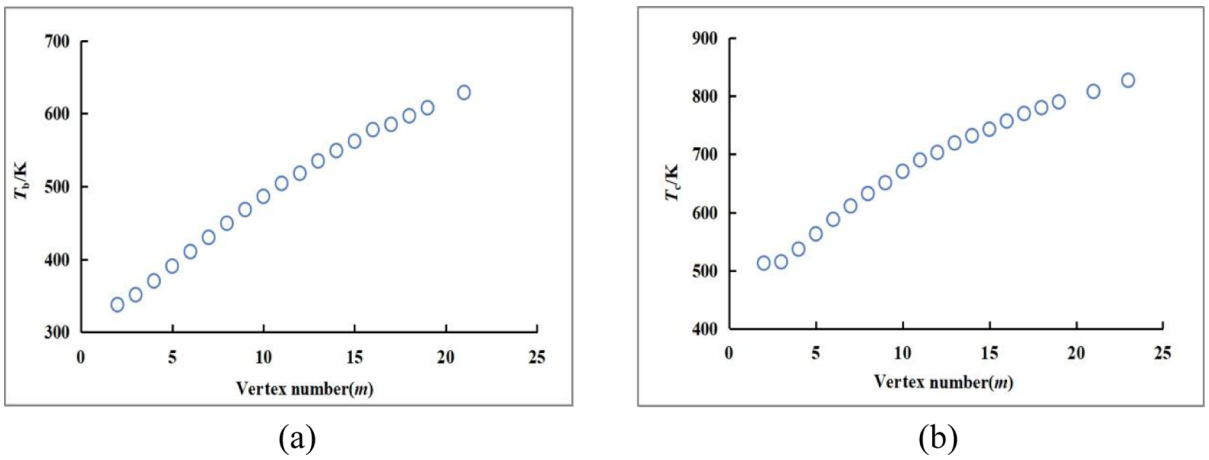

Figure 4. Plots of T_b (a) and T_c (b) versus the vertex number m for linear ROH.

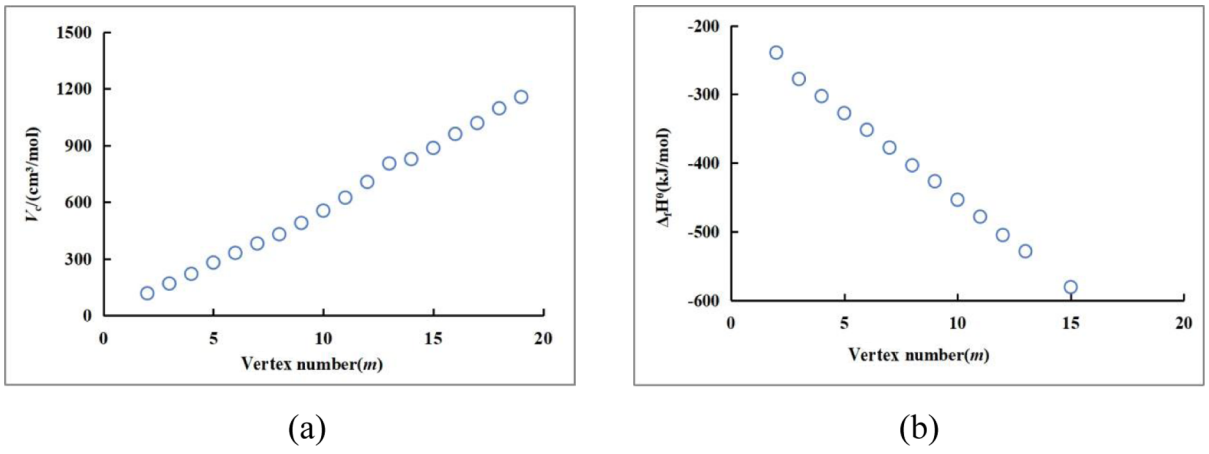

Figure 5. Plots of V_c (a) and $\Delta_f H^0$ (b) versus the vertex number m for linear ROH.

With the same way, the topological index of each structure should be based on linear aliphatic alcohols, since the meaning of PEI is the polarization effect of the OH on the carbon skeleton, excluding the O atoms. Therefore, PEI should be divided by the number of carbon atoms n, as shown in eq 9.

$$\Delta(\mathrm{APEI}) = \Delta\mathrm{PEI}/n = [(\mathrm{PEI})_{\mathrm{bran}} - (\mathrm{PEI})_{\mathrm{lin}}]/n \quad (9)$$

2.1.4.2. Hydroxyl Group Influencing Factor G_N. According to Cao's report,[16] in monosubstituted alkane RX, we think that the effect of the X group on the property of RX can be expressed by the ratio of group number to the number of carbon atoms, that is, $G_N = 1/n$. Thus, the effect of OH on the molecule ROH can be expressed as $G_N = 1/n$, where n is the number of carbon atom. As the carbon chain grows, the effect of OH on the properties of alcohols decreases. It implies that, for an aliphatic alcohol ROH, the effect of group OH can be negligible in the case of the carbon number of R approaching infinity. Therefore, G_N is used to describe the magnitude of the influence of OH on the molecular structure.

These calculated molecular descriptors, m, S_{VNE}, OEI, IMPI, APEI, Δ(AOEI), Δ(AIMPI), Δ(APEI), and G_N are listed in the Supporting Information.

2.1.5. General Equation Expressing the Properties of Aliphatic Alcohols. Herein, six molecular descriptors, involving the m, S_{VNE}, Δ(AOEI), Δ(AIMPI), Δ(APEI), and G_N, are used to establish a general equation of the physicochemical properties of aliphatic alcohols.

It should noted that the physicochemical properties of aliphatic alcohols,[1,17−20] such as boiling point[21] and critical temperature, show a nonlinear change trend with the vertex number, as shown in Figure 4. According to the method reported by Cao et al.,[16] we proposed eq 10 to express the nonlinear change properties of ROH, where a, b, c, d, e, f, and g are the coefficients, and are obtained by regression analysis.

$$\ln(P_{(m)}) = a + b(m) + c(S_{\mathrm{VNE}}) + d(\Delta(\mathrm{AOEI})) + e(\Delta(\mathrm{AIMPI})) + f(\Delta(\mathrm{APEI})) + g(G_{\mathrm{N}}) \quad (10)$$

The physicochemical properties of aliphatic alcohols, such as critical volume and enthalpy of formation of liquid, show a linear change trend with the vertex number increase, as shown in Figure 5. Thus, we proposed eq 11 to express the linear change properties of ROH, where a, b, c, d, e, f and g are the coefficients and are obtained by regression analysis.

$$P_{(m)} = a + b(m) + c(S_{\mathrm{VNE}}) + d(\Delta(\mathrm{AOEI})) + e(\Delta(\mathrm{AIMPI})) + f(\Delta(\mathrm{APEI})) + g(G_{\mathrm{N}}) \quad (11)$$

2.2. Verification and Application of the Equations. *2.2.1. Correlation with the Nonlinear Properties of Aliphatic Alcohols.* It was observed that the boiling point (T_b), refractive index (n_D), density (ρ), critical temperature (T_c), and critical pressure (P_c) show a nonlinear trend as the vertex number

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Table 2. Equations for Nonlinear Change Properties of the Aliphatic Alcohol Model: $\ln(P_{(m)}) = a + b(m) + c(S_{VNE}) + d(\Delta(AOEI)) + e(\Delta(AIMPI)) + f(\Delta(APEI)) + g(G_N)$

no	property	equations
1	T_b	$\ln(T_b) = 5.3092 + 0.008154(m) + 0.2689(S_{VNE}) + 0.08759(\Delta(AOEI)) - 0.2087(\Delta(AIMPI)) - 0.9802(\Delta(APEI)) + 0.2328(G_N)$
2	n_D	$\ln(n_D) = 0.2573 - 0.002583(m) + 0.04522(S_{VNE}) + 0.03075(\Delta(AOEI))+ 0.06246(\Delta(AIMPI)) - 0.07090(\Delta(APEI)) - 0.01365(G_N)$
3	T	$\ln(T_c) = 5.6437 - 0.001438(m) + 0.2973(S_{VNE}) + 0.09307(\Delta(AOEI)) - 0.03798(\Delta(AIMPI)) - 1.288(\Delta(APEI)) - 0.3040(G_N)$
4	P_c	$\ln(P_c) = 2.5110 - 0.04687(m) - 0.3943(S_{VNE}) + 0.2955(\Delta(AOEI))+ 1.0100(\Delta(AIMPI)) - 1.6027(\Delta(APEI)) + 0.06173(G_N)$
5	P	$\ln(\rho) = -0.2799 - 0.000652(m) + 0.03250(S_{VNE}) + 0.1563(\Delta(AOEI))+ 0.2793(\Delta(AIMPI)) - 0.1294(\Delta(APEI)) + 0.01216(G_N)$
6	$C_{p,nonlinear}$[a]	$\ln(C_p) = 3.1516 + 0.001034(m) + 0.9304(S_{VNE}) + 0.1186(\Delta(AOEI))+ 0.1897(\Delta(AIMPI)) + 4.1166(\Delta(APEI)) + 0.3134(G_N)$

[a] $C_{p,nonlinear}$ indicates that the C_p is treated as nonlinear change.

increase. Using eq 10 as the model equation, the quantitative correlation equations for the nonlinear properties of aliphatic alcohols can be obtained via employing the multiple regression analysis method, and the obtained equations are listed in Table 2.

In the study of Cao et al.,[9,21] the heat capacities (C_p) of alkanes and aliphatic amines were treated as nonlinear change properties. In this work, the heat capacities of aliphatic alcohols were treated by both nonlinear and linear changes, and the two regression results were compared.

2.2.2. Correlation with the Linear Properties of Aliphatic Alcohols. It was observed that the enthalpy of formation (Δ_fH^θ) and critical volume (V_c) show a linear trend with the vertex number increase. Using eq 11 as the model equation, the quantitative correlation equations for the linear properties of aliphatic alcohols can be obtained via employing the multiple regression analysis method, and the obtained equations are listed in Table 3. In Section 2.2.1, nonlinear regression was performed for the heat capacity of aliphatic alcohols; in this section, it was performed with a linear regression, and the two regression results were compared.

Table 3. Equations for Linear Change Properties of the Aliphatic Alcohol Model: $P_{(m)} = a + b(m) + c(S_{VNE}) + d(\Delta(AOEI)) + e(\Delta(AIMPI)) + f(\Delta(APEI)) + g(G_N)$

no	property	Equations
1	$C_{p,linear}$[a]	$C_p = -50.6192 + 29.390(m) + 32.9547(S_{VNE}) + 66.126(\Delta(AOEI)) + 124.57(\Delta(AIMPI)) + 939.61(\Delta(APEI)) + 40.789(G_N)$
2	V_c	$V_c = 81.9682 + 70.1230(m) - 72.2758(S_{VNE}) - 72.4626(\Delta(AOEI)) - 56.4788(\Delta(AIMPI)) - 114.177(\Delta(APEI)) - 32.3160(G_N)$
3	Δ_fH^θ	$\Delta_fH^\theta = -251.15 - 27.378(m) + 23.9766(S_{VNE}) + 33.676(\Delta(AOEI)) - 200.288(\Delta(AIMPI)) + 15.9814(\Delta(APEI)) + 42.4146(G_N)$

[a] $C_{p,linear}$ indicates that the C_p is treated as linear change.

Table 4 summarizes the statistical tests of the corresponding estimation models for each property of aliphatic alcohols, in which N, S, R, F, AAE, and AAPE represent the number of experimental data points, standard error, correlation coefficient, Fisher significance test, average absolute error, and average absolute percentage error, respectively. In addition, the no. 6 and no. 7 of Table 4 show that the error of heat capacity is smaller for dealing with it as nonlinear change than dealing with it as linear change, indicating that heat capacity treated as nonlinear change is more suitable. In Table 4, the AAPE between the experimental and predicted values of all properties is less than 2.0%, indicating that the constructed models (eqs 10 and 11) are reliable.

We also noted that DIPPR has a very sophisticated equation for evaluating properties of organic compounds. Recently, Bloxham et al.[22] gave a good introduction for "proper use of the DIPPR 801 Database". Herein, they pointed out that DIPPR assigns nine quantized uncertainty levels (%) to any property value, namely, <0.2%, <1%, <3%, <5%, <10%, <25%, <50%, <100%, and >100%. Where, the first three best uncertainty levels are <0.2%, <1%, and <3%. Table 4 of this work shows that the AAPE values of T_b, n_D, T_c, ρ, and Δ_fH^θ all are less 1%, others are less 2%, being in lower uncertainty levels.

In this work, for the T_b of aliphatic alcohols, the AAE and AAPE are 2.93 K and 0.66%, respectively. They are less than the AAE = 4.4 K and AAPE = 1.01% reported by Cao et al.[8] in 2022. It means that the accuracy of the equation of T_b in Table 2 (no. 1) is higher than that of eq 2.

2.2.3. Relationship between Properties of Aliphatic Alcohols. From eqs 10 and 11, we noted that the linear and nonlinear change properties of aliphatic alcohols all can be expressed by the same parameters m, S_{VNE}, Δ(AOEI), Δ(AIMPI), Δ(APEI), and G_N, which means that the different properties of aliphatic alcohols can be connected to each other via using the above six molecular descriptors.

Table 4. Accuracy of the Correlation Equations for the Properties of Aliphatic Alcohols

no	property	N	R	S	F	AAE	AAPE (%)
1	T_b	144	0.9966	0.00855	3360.83	2.93	0.66
2	n_D	63	0.9892	0.00205	427.01	0.002	0.14
3	T_c	54	0.9992	0.00525	4907.25	2.17	0.36
4	P_c	50	0.9988	0.02041	2971.13	0.05	1.42
5	ρ	59	0.9471	0.00447	75.46	0.003	0.32
6	$C_{p,nonlinear}$	23	0.9990	0.01981	1397.52	2.89	1.19
7	$C_{p,linear}$	23	0.9979	6.251	642.54	3.94	1.76
8	V_c	52	0.9989	11.44	3437.00	7.90	1.69
9	Δ_fH^θ	29	0.9980	5.212	901.88	3.06	0.81

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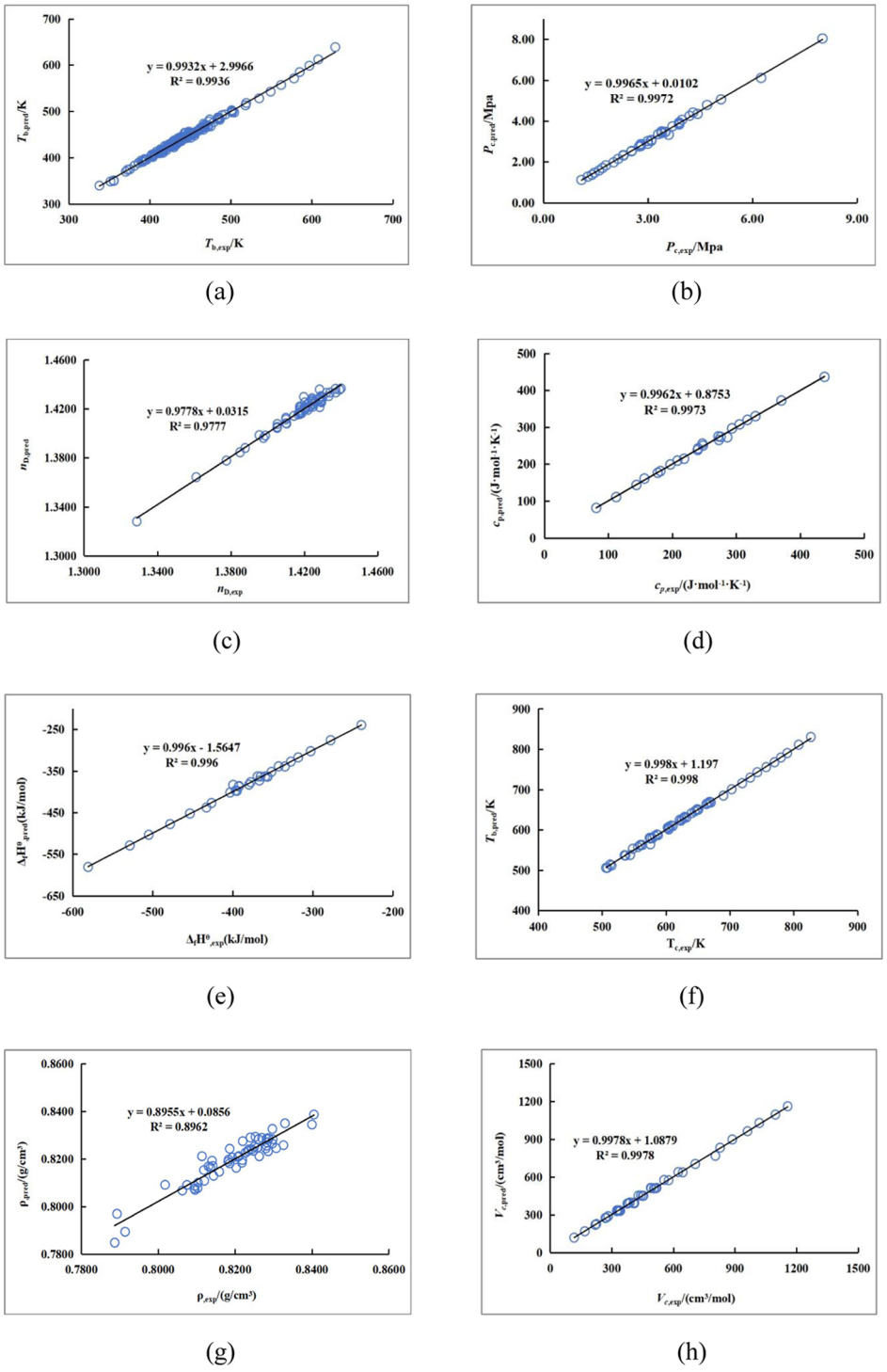

Figure 6. Plots of experimental versus calculated (a) T_b, (b) P_c, (c) n_D, (d) C_p, (e) $\Delta_f H^\theta$, (f) T_c, (g) ρ, and (h) V_c values of aliphatic alcohols.

2.2.3.1. Relationship between Nonlinear Change Properties of Aliphatic Alcohols. If one nonlinear change property of aliphatic alcohol is $P(m)$ (e.g., critical temperature) and another nonlinear change property is $P'(m)$ (e.g., boiling point), eq 12 can be theoretically deduced from eq 10, the following is the derivation

$$\begin{aligned}&[\ln(P_{(m)}) - \ln(P'_{(m)})]\\ &= (a - a') + (b - b')(m) + (c - c')(S_{VNE})\\ &\quad + (d - d')(\Delta(AOEI)) + (e - e')(\Delta(AIMPI))\\ &\quad + (f - f')(\Delta(APEI)) + (g - g')(G_N)\\ &= a_r + b_r(m) + c_r(S_{VNE}) + d_r(\Delta(AOEI))\\ &\quad + e_r(\Delta(AIMPI)) + f_r(\Delta(APEI)) + g_r(GN)\end{aligned}$$

Thus

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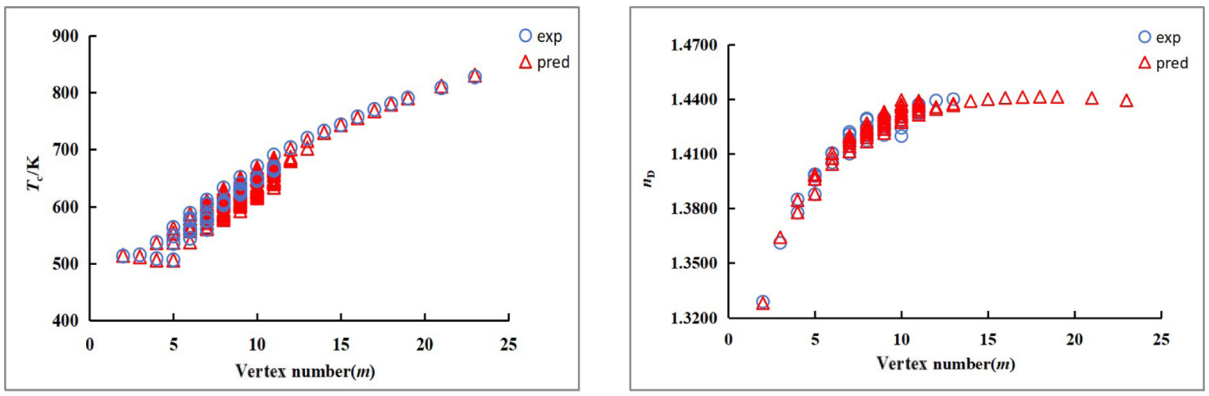

Figure 7. Plots of experimental (○) and predicted (Δ) values versus the vertex number (m) for the boiling point (a) and refractive index (b) of aliphatic alcohols.

$$\ln(P_{(m)}) = a_r + b_r(m) + c_r(S_{VNE}) + d_r(\Delta(AOEI)) + e_r(\Delta(AIMPI)) + f_r(\Delta(APEI)) + g_r(G_N) + \ln(P'_{(m)}) \quad (12)$$

For the two specific physicochemical properties of aliphatic alcohols, $P(m)$ and $P'(m)$, the parameters a_r, b_r, c_r, d_r, f_r, g_r, a_s, b_s, c_s, d_s, f_s, and g_s can be obtained by regression analysis.

2.2.3.2. Relationship between Nonlinear and Linear Change Properties of Aliphatic Alcohols. If one nonlinear change property of aliphatic alcohols is $P(m)$ (e.g., boiling point) and another linear change property is $P'_{LC}(m)$ (e.g., critical volume), eq 13 can be obtained from eqs 10 and 11.

$$P'_{LC(m)} = a_s + b_s(m) + c_s(S_{VNE}) + d_s(\Delta(AOEI)) + e_s(\Delta(AIMPI)) + f_s(\Delta(APEI)) + g_s(G_N) - \ln(P_{(m)}) \quad (13)$$

2.2.4. Prediction of Properties of Aliphatic Alcohols. The equations in Tables 2 and 3 can be used to calculate the physicochemical properties of aliphatic alcohols. The AAE and AAPE values between the calculated values and the experimental values are shown in Table 4. Figure 6 shows the plots of experimental properties versus the calculated values. Table 4 and Figure 6 show that the errors are small, so these equations can be used to predict the properties of ROH without experimental values. Figure 7a,b shows plots of experimental (○) and predicted (Δ) values versus the vertex number (m) for the boiling point (T_b) and refractive index (n_D) of ROH, respectively. These predicted and experimental values, involving 15 normal boiling points, 96 refractive indexes, 105 critical temperatures, 109 critical pressures, 100 liquid densities, 136 heat capacities, 107 critical volumes, and 130 gas enthalpies of formation of liquid, are listed in the Supporting Information.

The relationship between the properties of aliphatic alcohols is discussed in Section 2.2.3. When we collected the experimental data of various physicochemical properties of aliphatic alcohols, we noted that there are more data of boiling points and their experimental errors are small. If the boiling points of aliphatic alcohols are used as one of the variables to connect with other linear properties, or nonlinear properties, then the predicted values should also be reliable.

2.3. Preliminary Investigation on the General Model of Aliphatic Alcohols-Amines. *2.3.1. Comparison on General Models of Aliphatic Alcohols-Amines.* In this work, the general model for the nonlinear change properties of aliphatic alcohols is shown in eq 10. While Cao et al.[16] proposed eq 14 as a general model for expressing the nonlinear change properties of aliphatic amines.

$$\ln(P_{(n)}) = a + b(n) + c(S_{CNE}) + d(\Delta(AOEI)) + e(PEI) + f((\Delta APEI)) + g(G_N) \quad (14)$$

We wanted to know if eq 10 could be used to correlate the physicochemical properties of aliphatic primary amines; thus, we collected the boiling point values of 36 aliphatic primary amines. Using eq 10 as a model equation, we performed a regression analysis. The correlation coefficient R is 0.9998 and the standard error S is 0.00511. In the case of eq 14 as the model equation, the correlation coefficient R is 0.9998 and the standard error S is 0.00567. These results show that both eqs 10 and 14 can be employed to establish a general model of the boiling point of aliphatic primary amines, but eq 10 gives better results for both alcohols and amines. It means that eq 10 can be used as the basis for the combination of the general models of aliphatic alcohols and aliphatic primary amines, which is what people have been investigating and looking forward to establishing a general expression for the physicochemical properties of different kind of compounds.

2.3.2. Establishing the General Model of Aliphatic Alcohols-Amines. Aliphatic alcohols (ROH) differ from aliphatic primary amines (RNH_2) in terms of functional groups, specifically, the electronegativity of the OH and amino group (NH_2) is different from each other, and the intramolecular polarization effect of OH and NH_2 on alkyl R is also different from each other. In addition, there are differences in the changes caused by OH and NH_2 for specific physicochemical properties. While, when the OH and NH_2 are replaced by CH_3, respectively, the ROH and RNH_2 will have the same molecular skeleton and molecular graph. It means that the properties of both ROH and RNH_2 are influenced by the vertices and molecular skeleton in the same way, with only the influence of functional groups OH and NH_2 being different. If we can find the feature contributions of groups OH and NH_2 to the properties of ROH and RNH_2, respectively, we can establish a general equation to correlate

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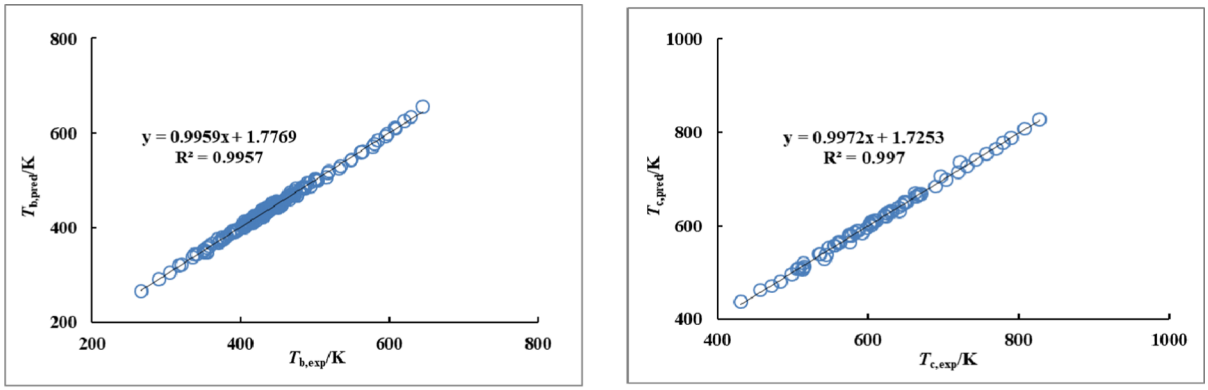

Figure 8. Plots of experimental versus calculated T_b (a) and T_c (b) values of both ROH and RNH_2.

their properties of them. In this paper, the boiling point and critical temperature of aliphatic alcohols and aliphatic primary amines are taken as examples to explore whether the general estimation models of different kind of compounds can be established.

2.3.3. Addition of Molecular Descriptors. 2.3.3.1. Physicochemical Characteristic Parameter (ΔPx). Here, we proposed a parameter ΔPx to represent the contribution of the X group to the specific physicochemical property of the compound RX, that is, $\Delta Px = P_{(Et\text{-}X)} - P_{(Et\text{-}H)}$, where P represents a certain property of the compound RX, X represents the functional group attached to the alkyl group; for example, X is OH in aliphatic alcohols, and X is NH_2 in aliphatic primary amines. When an H atom of ethane (Et-H) is replaced by an OH group, the effect of adding OH on the boiling point of ethane can be roughly expressed by the difference between boiling point T_b of ethanol (EtOH) and that of ethane (Et-H), and the effect of adding a OH on the critical temperature T_c of ethane can be roughly expressed by the difference between critical temperature T_c of EtOH and that of Et-H. The same goes for amino group NH_2.

2.3.3.2. Intramolecular Polarization Characteristic Parameter ($G_N \times \mu_{ind}$). The polarization between the carbon skeleton and the functional group can be expressed by intramolecular charge-induced dipole μ_{ind},[23] that is, $\mu_{ind} = \chi_X \times PEI(R)$, where χ_X is the electronegativity of group X and PEI(R) is the PEI of the alkyl R. The χ_X values of groups OH and NH_2 are 3.26 and 2.80,[24] respectively. The effect of this intramolecular polarization on the properties of the compound is related to the length of the carbon chain. The longer the carbon chain, the smaller the effect proportion of this polarization on the property of RX will be. Therefore, we use $G_N \times \mu_{ind}$ to further distinguish NH_2 from OH, in which $G_N = 1/n$.

2.3.4. General Models of Aliphatic Alcohols-Amines. On the basis of eq 10, adding the above two molecular structure characteristic parameters, ΔPx and $G_N \times \mu_{ind}$ to eq 10, we can obtain eq 15, which is a general model of aliphatic alcohols-amines for nonlinear change properties.

$$\ln(P_{(m)}) = a + b(m) + c(S_{VNE}) + d(\Delta(AOEI)) + e(\Delta(AIMPI)) + f(\Delta(APEI)) + g(G_N) + h(\Delta P_x) + i(G_N \times \mu_{ind}) \quad (15)$$

Taking the boiling point of ROH and RNH_2 as example, we collected the experimental values of the boiling points of 36 RNH_2[16,25] and 144 ROH. Using eq 15 as a model equation, eq 16 was obtained. The standard error S and correlation coefficient R of eq 16 are 0.0093 and 0.9979, respectively. The AAE and AAPE values between the experimental and calculated values are 3.15 K and 0.71%, respectively. Figure 8a is the plot of experimental boiling points versus the calculated values.

$$\ln(T_b) = 4.5385 + 0.00428(m) + 0.3187(S_{VNE}) + 0.09451(\Delta(AOEI)) - 0.2142(\Delta(AIMPI)) - 1.1226(\Delta(APEI)) + 0.2351(G_N) + 0.003968(\Delta P_x) + 0.02218(G_N \times \mu_{ind})$$
$$R = 0.9979,\ S = 0.0093,\ F = 14963.03,\ N = 180 \quad (16)$$

Taking critical temperature of ROH and RNH_2 as another example, we collected the experimental values of the critical temperatures of 17 RNH_2[16,25] and 54 ROH. Using eq 15 as the model equation, eq 17 was obtained. The standard error S and correlation coefficient R of eq 17 are 0.0085 and 0.9983, respectively. The AAE and AAPE values between the experimental and calculated values are 3.47 K and 0.58%, respectively. Figure 8b is the plot of experimental critical temperatures versus the calculated values.

$$\ln(T_c) = 5.2012 - 0.00034(m) + 0.2753(S_{VNE}) + 0.09222(\Delta(AOEI)) - 0.1183(\Delta(AIMPI)) - 1.1746(\Delta(APEI)) + 0.211(G_N) + 0.00238(\Delta P_x) + 0.012(G_N \times \mu_{ind})$$
$$R = 0.9983,\ S = 0.0085,\ F = 2334.28,\ N = 71 \quad (17)$$

In summary, through establishing a general model of boiling point and critical temperature of both ROH and RNH_2, the results show that the correlation coefficient is good, and the error between the predicted value and the experimental value is small. It can be considered that eq 15 can be generalized to establish a general equation for estimating the other physicochemical properties of both aliphatic primary amines and aliphatic alcohols.

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3. CONCLUSION

The property changes of aliphatic alcohols can be divided into two categories: nonlinear change and linear change, both of which can be expressed by six molecular descriptors m, S_{VNE}, Δ(AOEI), Δ(AIMPI), Δ(APEI), and G_N. The general model of nonlinear change properties of aliphatic alcohols is expressed in eq 10, while their general model of linear change properties is expressed in eq 11. The linear and nonlinear change properties of aliphatic alcohols all have a good correlation with the six molecular descriptors, which can be used to predict the physicochemical properties of aliphatic alcohols without experimental measurements, and the obtained general equations can also be used to correlate different physicochemical properties of aliphatic alcohols.

The boiling point and critical temperature of both aliphatic alcohols and aliphatic primary amines can be expressed by a general equation via adding two group feature parameters. It provides a new method to establish a general equation for estimating the physicochemical properties of both aliphatic primary amines and aliphatic alcohols.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c09457.

Experimental and predicted physicochemical property values of aliphatic alcohols and calculated molecular descriptors of aliphatic alcohols (PDF)

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Notes

The authors declare no competing financial interest.

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■ NOMENCLATURE

P_c	critical pressure
T	temperature
T_c	critical temperature
T_b	boiling point
n_D	refractive index
ρ	liquid density
C_p	liquid heat capacity
V_c	critical volume
$\Delta_f H^\theta$	enthalpy of formation of liquid
m	vertex number
n	carbon atom number
N	experimental data points
S	standard error
R	correlation coefficient
F	Fisher significance test
AAE	average absolute error
AAPE	average absolute percentage error
S_{CNE}	sum of the carbon number effect
S_{VNE}	sum of the vertex number effect
OEI	odd−even index
IMPI	intramolecular polarization effect index
PEI	polarization effect index
AOEI, AIMPI, and APEI	average values of OEI, IMPI, and PEI, respectively
G_N	group influencing factor (the ratio of group number to the number of carbon atoms)
μ_{ind}	intramolecular charge-induced dipole
χ_X	X group electronegativity
ΔPx	contribution of the X group to the specific property

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