Position Group Contribution Method for the Prediction of Critical Volume of Organic Compounds

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In this study, a combined approach of group contribution and position distribution function is presented to estimate the critical volume of a variety of pure organic compounds involving a carbon chain from C2 to C18. The results indicate that our model provides very satisfactory results, and the deviation from the most reliable experimental data is not more than 2.1 %. The overall average absolute difference for critical volume V_c predictions of 219 organic compounds is 8.8 $cm^3 \cdot mol^{-1}$ and 2.1 % means relative derivation, which is compared to 26.5 $cm^3 \cdot mol^{-1}$ and 6.0 % with the method of Joback and 23.5 $cm^3 \cdot mol^{-1}$ and 5.6 % with the method of Constantinou and Gani. The higher prediction accuracy of the proposed method shown in our previous works and this work suggests that it is possible to use a similar framework to predict the three critical properties, T_c, P_c, and V_c of organic compounds containing various functionalities.

Introduction

Critical properties are important to predict various thermodynamic properties using the principle of corresponding states. Unfortunately, experimental critical properties data of organic compounds are limited due to the fact that many compounds become unstable during measurements near or even far from the vicinity of the critical point. In such conditions, mathematical models can be used to provide a reasonable estimate of these properties. The method used in estimating critical property data in various applications including chemical process design is the group contribution method. Jensen et al.,[1] Joback and Reid,[2] Somayajulu,[3] and Li et al.[4] proposed such methods for the prediction of a variety of thermodynamic properties (e.g., vapor pressure, critical temperature, critical pressure, boiling point) of organic compounds.

However, most group contribution methods have a serious problem that they cannot distinguish among structural isomers. To overcome this problem, many researchers have tried to improve group contribution methods. Constantinou and Gani,[5] Marrero and Gani,[6] and Olsen and Nielsen[7] developed methods which perform estimations at different levels. Recently, Nannoolal et al.[8] developed some new equations for the prediction of critical parameters, and our laboratory proposed a position group contribution method for the prediction of critical parameters of organic compounds that requires only the knowledge of their chemical structure.[9,10]

As our preliminary work on the critical temperature and the critical pressure showed significant improvements with respect to the published methods, it was decided to also invest further effort into the development of a new group contribution method for critical volume.

Method Proposed in This Work

Experimental Data. A total of 219 compounds were used for the determination of group contributions, which include linear and branched alkanes (48) and cycloalkanes (11), alkenes (11), aromatics (9), ketones (41), aldehydes (8), alcohols and ether oxides (36), acids (9), esters (20), amines and pyridines (17), and nitriles and alkane thiols (9).

The sources of experimental data were from a series of critical compilation reviews by the critical properties group of the IUPAC I: two on thermodynamics, and the works were published in *J. Chem. Eng. Data* by Ambrose,[11,12] Tsonopoulos,[13,16,18] Gude,[14] Daubert,[15] Kudchadker,[17] and Marsh et al.[19,20] Critical data were also obtained from a compilation of organic property data by Ma.[21]

Position Group Contributions for the Critical Volume. The critical volume function is constructed by all groups' contribution as well as by the position correlation factor. The position correlation factor was used to take into account longer distance interactions, which could distinguish most isomers including *cis*- and *trans*- or *Z*- and *E*-structures of organic compounds for their thermodynamics properties.

Here, the position distribution function for the estimation of critical volume is expressed as

$$V_C/\mathrm{cm^3 \cdot mol^{-1}} = V_0 + \sum_i A_i N_i + \sum_j A_j \tanh(N_j/N) + \sum_k A_k P_k + a_1 \exp(1/M) + a_2 \exp(1/N) \quad (1)$$

$$N = \sum_i N_i + \sum_j N_j \quad (2)$$

Parameter A_i or A_j stands for i or j group contributions, N_i for the number of each group that the carbon element forms the center of the group in the molecular formula, N_j for the number of each group that the noncarbon element forms the center, N for the total number of groups, P_k for the position correlation factor, and a_1, a_2 for parameters of the model. The set of

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Table 1. Position Group Contributions for the Prediction of V_C[a]

group	A	group	A
	$cm^3 \cdot mol^{-1}$		$cm^3 \cdot mol^{-1}$
C−(CH3)(H)3	28.836	C−(C)(Cl)(H)2	68.973
C−(CH2)(H)3	32.124	C−(C)2(Cl)(H)	78.093
C−(CH)(H)3	44.253	C−(C)(Cl)2(H)	68.266
C−(C)(H)3	39.010	C−(S)(H)3	41.775
C−(C)2(H)2	64.715	C−(C)(S)(H)2	62.527
C−(C)3(H)	78.892	C−(C)2(S)(H)	81.299
C−(C)4	102.700	C−(C)3(S)	105.706
Cd−(H)2	118.285	Cb−(N)	−378.326
Cd−(C)(H)	66.042	C−(N)(H)3	12.0841
C−(Cd)(C)(H)2	115.088	C−(C)(N)(H)2	71.040
C−(Cd)(H)3	79.600	C−(C)2(N)(H)	85.499
Cd−(C)2	−22.636	C−(C)3(N)	127.735
C−(Cd)(C)2(H)	137.840	C−(C)(CN)(H)2	141.376
Cd−(Cd)(H)	259.960	N−(CH3)(H)2	56.628
C−(O)(H)3	24.628	N−(CH2)(H)2	54.114
C−(CO)(H)3	63.932	N−(CH)(H)2	46.908
C−(C)(CO)(H)2	100.338	N−(cyclopenty)(H)2	−14.360
C−(C)2(CO)(H)	126.274	N−(cyclohexy)(H)2	−34.516
C−(C)3(CO)	182.117	N−(C)2(H)	367.7
C−(C)(O)(H)2	46.625	N−(C)3	1243.887
C−(C)2(O)(H)	60.101	N−(Cb)(H)2	2807.391
C−(C)3(O)	82.642	N−(C)2 correction	−27.248
CO−(CH3)(O)	112.500	N−(C)3 correction	−138.294
CO−(CH2)(O)	170.243	NI−(Cb)2	−187.90
CO−(CH)(O)	209.270	S−(C)(H)	207.134
CO−(O)(H)	68.875	Cl−(C)	164.290
CO−(C)(H)	15.324	ortho correction[b]	−2.268
CO−(C)2	−15.991	meta correction[b]	11.567
CO−(O)(Cd)	897.969	cyclopentane correction	−104.566
Cb−(H)	30.627	cyclohexane correction	−92.337
Cb−(C)	15.102	C_{ob}[c]	6.466
C−(Cb)(H)3	51.359	C_{mb}[c]	6.466
C−(Cb)(C)(H)2	52.579	C_{pb}[c]	6.163
C−(Cb)(C)2(H)	93.578	cyclopropane correctiom[d]	90.607
C−(Cb)(C)3	112.641	−(CH)< position correction[d]	−5.060
Cb−(O)	2803.033	>(C)< position correction[d]	−8.151
O−(Cb)(H)	−3476.48	double bond position correction[d]	−2.441
O−(C)(H)	72.835	hydroxyl position correction[d]	4.369
O−(C)2	372.475	benzene correction[d]	210.031
O−(CO)(CH3)	221.203	*trans* or *cis* structure correction[d]	−2.068
O−(CO)(CH2)	409.728	carbonyl position correction[d]	1.684
O−(CO)(CH)	405.810	phenol position correction[d]	28.993
C−(C)(Br)(H)2	118.396	a_2	46.240
C−(C)2(Br)(H)	161.123	a_1	989.257
V_0	−1011.117		

[a] Notice: The first symbol represents the element that forms the center of the group. The symbols between parentheses represent the elements to which it is linked. Usual symbols are used to represent the elements in their normal valence state. Elements in other valence states are distinguished by using additional characters; furthermore, different symbols represent multiple bonded carbons, depending on the element at the other end of the multiple bond: Cd, carbon forming a double bond with another carbon; Cb, carbon involved in a benzene or a pyridine ring; CO, C═O group; CN, C≡N group; N_I, nitrogen of the imide (C═N−) function. Also used for the nitrogen of pyridine derivatives. The pyridine ring is considered as formed of five Cb and one N_I. trans or cis correction: cis-structure correction is 1 and trans structure is −1. [b] Ortho and meta corrections consider interactions between alkyl chains through a benzene ring. [c] Corrections for pyridines: C_{ob}, C_{mb}, and C_{pb} pyridine corrections take into account alkyl ligands in position ortho, meta, and para with respect to the N element, respectively. [d] Position correction.

contributions that allowed us to minimize the residual estimation difference was then computed by regression. V_0 is −1011.117 $cm^3 \cdot mol^{-1}$, and M is molecular weight. According to the IUPAC nominating method, we draw the structures and assign the P_k values for the relevant positional correction. Table 1 reports the values computed for the group contributions A_i, and our method developed is applicable only to comparatively low-molar-mass compounds involving the carbon chain from C2 to C18.

Table 2. Comparison of V_C Predicted with Our Method and with the Methods of Joback and Constantinou for Various Class Organic Compounds[a]

chemical family	no. of compounds	Joback		Constantinou		this work	
		AAD		AAD		AAD	
		$cm^3 \cdot mol^{-1}$	$100\bar{\delta}$	$cm^3 \cdot mol^{-1}$	$100\bar{\delta}$	$cm^3 \cdot mol^{-1}$	$100\bar{\delta}$
alkanes	48	21.4	3.2	21.3	3.2	11.0	2.1
cycloalkanes	11	4.2	1.2	18.5	5.9	11.6	4.5
alkenes	11	4.0	1.2	5.7	2.0	3.2	1.1
aromatics	9	4.9	1.3	3.8	1.0	12.2	3.2
ketones	41	29.9	4.1	36.3	5.5	5.3	1.0
aldehydes	8	14.4	4.2	10.2	3.1	8.5	1.9
alcohols & ether oxides	36	57.5	13.8	13.3	3.1	6.8	1.6
acids	9	12.4	2.8	9.0	2.1	14.1	4.0
esters	20	22.4	6.2	22.9	6.5	11.7	3.4
amines and pyridines	17	18.7	6.2	17.7	6.0	3.3	1.2
nitriles & alkane thiols	9	26.8	8.4	23.7	7.1	11.3	3.5
overall	219	26.5	6.0	23.5	5.6	8.8	2.1

[a] AAD is the overall average absolute difference and $\bar{\delta}$ is the average mean difference.

Results and Discussion

Prediction of Critical Volume. The results of the reference compounds obtained using the new position group contribution method were presented in detail in Table 3. To illustrate the application of the proposed method, a detailed procedure for the estimation of critical properties is given in Appendix A for the critical volume. Table 2 compares the critical volume predictions obtained using our method and previous methods to experimental data. Also, the overall average absolute difference (AAD) between experimental and predicted values for each group of molecules as well as the overall mean differences δ and the average mean differences $\bar{\delta}$ are summarized in Table 2.

$$\mathrm{AAD} = \frac{\sum |V_{\mathrm{c,exp}} - V_{\mathrm{C,pred}}|}{n} \tag{3}$$

$$\delta = \left| \frac{V_{\mathrm{c,exp}} - V_{\mathrm{C,pred}}}{V_{\mathrm{c,exp}}} \right| \tag{4}$$

$$\bar{\delta} = \frac{1}{N} \sum_{n} \left| \frac{V_{\mathrm{c,exp}} - V_{\mathrm{C,pred}}}{V_{\mathrm{c,exp}}} \right| \tag{5}$$

The performance of the new model has been compared with two well-known estimation methods from the literature, and the results indicate that the new model is significantly more reliable. Results presented in Table 2 show that the proposed method is more accurate than other methods for the critical volume. The AAD for critical volume V_c predictions of 219 organic compounds is 8.8 $cm^3 \cdot mol^{-1}$ and $\bar{\delta}$ is 2.1 %, which is compared to 26.5 $cm^3 \cdot mol^{-1}$ and 6.0 % with the method of Joback and 23.5 $cm^3 \cdot mol^{-1}$ and 5.6 % with the method of Constantinou and Gani. Results presented in Tables 3 prove that the predicted critical volume agrees well with the experimental results.

Uncertainty of the New Model. According to the F distribution function, the degree of confidence is calculated with the incomplete beta function which could be calculated from the gamma function. The results show that the correlation coefficient is 0.9946, the value of F distribution is 274.51, and the degree of confidence is 0.9990, which confirms the greater precision of our position group contribution method which can be used for the best estimation of the critical volume of organic compounds.

Table 3. Fully Predictive Estimations of Critical Volume V_C[a]

	V_c(exp)		this work		
compds	$cm^3 \cdot mol^{-1}$	ref	predict	D	100δ
ethane	145.5	12	146	0.0	0.0
propane	200	12	194	5.7	2.8
n-butane	255	12	248	6.6	2.6
2-methylpropane	259	15	256	2.8	1.1
n-pentane	311	12	307	4.2	1.3
2-methylbutane	306	15	303	3.5	1.1
2,2-dimethylpropane	307	15	291	16.1	5.3
n-hexane	368	12	367	0.6	0.2
2-methylpentane	368	15	363	4.9	1.3
3-methylpentane	368	15	346	22.0	6.0
2,2-dimethylbutane	358	15	345	13.4	3.7
2,3-dimethylbutane	361	15	354	7.2	2.0
n-heptane	428	12	429	1.2	0.3
2-methylhexane	421	15	425	3.9	0.9
3-methylhexane	404	15	408	3.8	0.9
3-ethylpentane	416	15	396	20.4	4.9
2,2-dimethylpentane	416	15	406	9.6	2.3
2,3-dimethylpentane	393	15	403	10.5	2.7
2,4-dimethylpentane	418	15	411	7.4	1.8
3,3-dimethylpentane	414	15	391	22.7	5.5
2,2,3-trimethylbutane	398	15	397	1.0	0.2
n-octane	492	12	492	0.2	0.0
2-methylheptane	488	15	487	0.5	0.1
3-methylheptane	464	15	470	6.3	1.4
4-methylheptane	476	15	465	10.8	2.3
3-ethylhexane	455	15	458	3.2	0.7
2,2-dimethylhexane	478	15	469	9.1	1.9
2,3-dimethylhexane	468	15	466	2.0	0.4
2,4-dimethylhexane	472	15	461	11.0	2.3
2,5-dimethylhexane	482	15	468	14.0	2.9
3,3-dimethylhexane	443	15	454	10.9	2.5
3,4-dimethylhexane	466	15	444	22.2	4.8
2-methyl-3-ethylpentane	442	15	454	11.9	2.7
3-methyl-3-ethylpentane	455	15	447	8.0	1.8
2,2,3-trimethylpentane	436	15	447	11.5	2.6
2,2,4-trimethylpentane	468	15	455	13.5	2.9
2,3,3-trimethylpentane	455	15	450	5.4	1.2
2,3,4-trimethylpentane	460	15	452	8.4	1.8
n-nonane	555	12	555	0.2	0.0
2-methyloctane			551		
4-ethyloctane			580		
2,2-dimethyloctane			607		
2,3-dimethyloctane			592		
2,4-dimethyloctane			587		
2,5-dimethyloctane			582		
2,6-dimethyloctane			577		
2,7-dimethyloctane			584		
3,3-dimethyloctane			580		
3,4-dimethyloctane			570		
3,5-dimethyloctane			565		
3,6-dimethyloctane			560		
4,4-dimethyloctane			572		
4,5-dimethyloctane			560		
4-propylheptane			580		
3-ethyl-2-methylheptane			580		
3-ethyl-3-methylheptane			573		
3-ethyl-4-methylheptane			558		
3-ethyl-5-methylheptane			553		
4-ethyl-2-methylheptane			575		
4-ethyl-3-methylheptane			558		
4-ethyl-4-methylheptane			571		
5-ethyl-2-methylheptane			570		
2,2,3-trimethylheptane			574		
2,2,4-trimethylheptane			569		
2,2,5-trimethylheptane			564		
2,2,6-trimethylheptane			571		
2,3,3-trimethylheptane			576		
2,3,4-trimethylheptane			566		
2,3,5-trimethylheptane			561		
2,3,6-trimethylheptane			568		
2,4,4-trimethylheptane			568		
2,4,5-trimethylheptane			556		
2,4,6-trimethylheptane			563		
2,5,5-trimethylheptane			560		
3,3,4-trimethylheptane			554		
3-methyloctane			533		
4-methyloctane			528		
2-ethylheptane			538		
3-ethylheptane			521		
4-ethylheptane			516		
2,2-dimethylheptane			532		
2,3-dimethylheptane			529		
2,4-dimethylheptane			524		
2,5-dimethylheptane			519		
2,6-dimethylheptane			526		
3,3-dimethylheptane			517		
3,4-dimethylheptane			507		
3,5-dimethylheptane			502		
4,4-dimethylheptane			509		
3-ethyl-2-methylhexane			517		
3-ethyl-3-methylhexane			510		
3-ethyl-4-methylhexane			495		
4-ethyl-2-methylhexane			512		
2,2,3-trimethylhexane			511		
2,2,4-trimethylhexane			505		
2,2,5-trimethylhexane			513		
2,3,3-trimethylhexane			513		
2,3,4-trimethylhexane			503		
2,3,5-trimethylhexane			510		
2,4,4-trimethylhexane			505		
3,3,4-trimethylhexane			490		
3,3-diethylpentane			552		
3-ethyl-2,2-dimethylpentane			498		
3-ethyl-2,3-dimethylpentane			506		
3-ethyl-2,4-dimethylpentane			503		
2,2,3,3-tetramethylpentane			494		
2,2,3,4-tetramethylpentane			496		
2,2,4,4-tetramethylpentane			493		
2,3,3,4-tetramethylpentane			498		
n-decane	624	12	618	5.8	0.9
2-methylnonane			614		
3-methylnonane			597		
4-methylnonane			592		
5-methylnonane			587		
3-ethyloctane			585		
3-ethyl-2,2-dimethylhexane			577		
3-ethyl-2,3-dimethylhexane			557		
3-ethyl-2,4-dimethylhexane			554		
3-ethyl-2,5-dimethylhexane			561		
3-ethyl-3,4-dimethylhexane			547		
4-ethyl-2,2-dimethylhexane			557		
4-ethyl-2,3-dimethylhexane			560		
4-ethyl-2,4-dimethylhexane			561		
4-ethyl-3,3-dimethylhexane			542		
2,2,3,3-tetramethylhexane			557		
2,2,3,4-tetramethylhexane			547		
2,2,3,5-tetramethylhexane			554		
2,2,4,4-tetramethylhexane			549		
2,2,5,5-tetramethylhexane			548		
2,2,4,5-tetramethylhexane			549		
2,3,3,4-tetramethylhexane			550		
2,3,3,5-tetramethylhexane			557		
2,3,4,4-tetramethylhexane			546		
2,3,4,5-tetramethylhexane			546		
3,3,4,4-tetramethylhexane			534		
3,3-dethyl-2-methylpentane			505		
3-ethyl-2,2,3-trimethylpentane			556		
3-ethyl-2,2,4-trimethylpentane			547		
3-ethyl-2,3,4-trimethylpentane			555		
2,2,3,3,4-pentamethylpentane			531		
2,2,3,4,4-pentamethylpentane			535		
n-undecane	689	12	682	7.2	1.0
n-dodecane	754	12	746	8.4	1.1
n-tridecane	823	12	810	13.4	1.6
n-tetradecane	894	12	874	20.4	2.3
n-pentadecane	966	12	938	28.2	2.9
n-hexadecane	1034	12	1002	32.0	3.1
n-heptadecane	1103	12	1066	36.7	3.3
n-octadecane	1189	12	1131	58.4	4.9
n-nonadecane			1195		

Table 3. Continued

	V_c(exp)		this work				V_c(exp)		this work		
compds	$cm^3 \cdot mol^{-1}$	ref	predict	D	100δ	compds	$cm^3 \cdot mol^{-1}$	ref	predict	D	100δ
3,3,5-trimethylheptane			549			cyclopropane	162	15	162	0.0	0.0
3,4,4-trimethylheptane			551			cyclobutane			314		
3,4,5-trimethylheptane			563			cyclopentane	259	15	268	8.8	3.4
3,4-diethylhexane			546			cyclohexane	308	15	341	32.5	10.6
3,3-diethylhexane			567			methylcyclopentane	318	15	317	1.0	0.3
methylcyclohexane	369	15	391	21.9	5.9	1-heptene	409	16	407	2.3	0.6
ethylcyclopentane	375	15	367	8.4	2.2	*cis*-2-heptene			409		
cis-1,2-dimethylcyclopentane			360			*trans*-2-heptene			413		
trans-1,2-dimethylcyclopentane			364			*cis*-3-heptene			410		
cis-1,3-dimethylcyclopentane			355			*trans*-3-heptene			414		
trans-1,3-dimethylcyclopentane			359			1-octene	468	16	466	2.1	0.4
1,1-dimethylcyclopentane			368			*cis*-2-octene			470		
1,1-dimethylcyclohexane			443			*trans*-2-octene			474		
cis-1,2-dimethylcyclohexane		21	435	25.0	5.4	*cis*-3-octene			470		
trans-1,2-dimethylcyclohexane		21	439	20.9	4.5	*trans*-3-octene			474		
cis-1,3-dimethylcyclohexane		21	430	13.9	3.3	*cis*-4-octene			468		
trans-1,3-dimethylcyclohexane		21	434	26.0	5.6	*trans*-4-octene			472		
cis-1,4-dimethylcyclohexane		21	425	35.2	7.6	1-nonene	526	16	526	0.4	0.1
trans-1,4-dimethylcyclohexane			429			1-decene	584	16	588	3.8	0.6
ethylcyclohexane			441			1-undecene			650		
n-propylcyclopentane			441			1-dodecene			712		
n-propylcyclohexane			504			1,3-butadiene	221	16	221	0.0	0.0
n-butylcyclopentane			492			benzene	256	13	279	22.9	8.9
n-butylcyclohexane			568			methylbenzene	316	13	325	8.6	2.7
n-pentylcyclopentane			555			1,4-dimethylbenzene	378	13	370	7.5	2.0
n-pentylcyclohexane			631			1,2-dimethylbenzene	370	13	368	1.8	0.5
n-hexylcyclopentane			619			1,3-dimethylbenzene	375	13	382	7.1	1.9
n-heptylcyclohexane			683			ethylbenzene	374	13	353	20.5	5.5
1-butene	240.8	16	245	4.4	1.8	1,2,3-trimethylbenzene			424		
cis-2-butene	233.8	16	238	4.3	1.8	1,2,4-trimethylbenzene			426		
trans-2-butene	237.7	16	242	4.5	1.9	1,3,5-trimethylbenzene			452		
1-pentene	298.4	16	295	3.7	1.2	1,2,3,4-tetramethylbenzene			480		
cis-2-pentene			294			1,2,3,5-tetramethylbenzene			494		
trans-2-pentene			298			1,2,4,5-tetramethylbenzene			482		
2-methyl-1-butene			292			1-methyl-2-ethylbenzene			398		
2-methyl-2-butene			291			1-methyl-3-ethylbenzene			412		
3-methyl-1-butene	304.9	16	309	4.2	1.4	1-methyl-4-ethylbenzene			400		
1-hexene	355.1	16	349	5.9	1.7	*n*-propylbenzene	440	13	415	25.3	5.8
cis-2-hexene			350			isopropylbenzene			447		
trans-2-hexene			355			1-methyl-2-isopropylbenzene			492		
cis-3-hexene			351			1-methyl-3-isopropylbenzene			506		
trans-3-hexene			355			1-methyl-4-isopropylbenzene			495		
2-methyl-1-hexene			399			*n*-butylbenzene	497	13	476	20.5	4.1
3-methyl-1-hexene			394			*sec*-butylbenzene			497		
4-methyl-1-hexene			380			*tert*-butylbenzene	492	21	492	0.0	0.0
n-pentylbenzene	550	21	539	11.2	2.0	5-dodecanone	759	17	759	0.2	0.0
n-hexylbenzene	593	21	601	8.4	1.4	6-dodecanone	762	17	760	1.5	0.2
n-heptylbenzene			664			2-tridecanone	820	17	814	6.0	0.7
butanone	267	17	247	19.8	7.4	3-tridecanone	823	17	820	3.5	0.4
2-pentanone	321	17	307	13.5	4.2	4-tridecanone	823	17	821	1.8	0.2
3-pentanone	331	17	313	18.0	5.4	5-tridecanone	826	17	823	3.1	0.4
3-methyl-2-butanone	308	17	310	1.9	0.6	6-tridecanone	826	17	825	1.4	0.2
2-hexanone	377	17	369	7.8	2.1	7-tridecanone	830	17	826	3.7	0.4
3-hexanone	378	17	375	3.3	0.9	2-tetradecanone	896	17	878	17.8	2.0
3,3-dimethyl-2-butanone	382	17	382	0.0	0.0	3-tetradecanone	896	17	884	12.3	1.4
4-methyl-2-pentanone			471			4-tetradecanone	900	17	885	14.6	1.6
2-heptanone	436	17	432	4.2	1.0	7-tetradecanone	904	17	890	13.5	1.5
3-heptanone	433	17	437	4.3	1.0	propanal	204	17	199	5.1	2.5
4-heptanone	434	17	439	5.0	1.2	butanal	258	17	254	4.1	1.6
2-octanone	497	17	495	2.1	0.4	1-pentanal	313	17	313	0.2	0.1
3-octanone	497	17	500	3.4	0.7	1-hexanal	378	17	374	4.5	1.2
4-octanone	497	17	502	5.1	1.0	1-heptanal	434	17	435	1.4	0.3
2-methyl-3-hexanone			445			1-octanal	488	17	498	9.9	2.0
5-methyl-2-hexanone			412			1-nonanal	543	17	561	17.9	3.3
2,4-dimethyl-3-pentanone			442			1-decanal	599	17	624	25.3	4.2
2-methyl-3-heptanone			485			2-methylpropanal			261		
5-methyl-3-heptanone			470			2-methylhexanal			431		
2,5-dimethyl-3-hexanone			488			3-methylhexanal			414		
5-nonanone	560	17	567	7.2	1.3	ethanol	168	14	171	2.9	1.7
4-nonanone	560	17	566	5.5	1.0	1-propanol	218	14	220	1.8	0.8
3-nonanone	560	17	564	3.9	0.7	2-propanol	222	14	229	7.3	3.3
2-nonanone	560	17	558	1.6	0.3	1-butanol	274	14	275	1.0	0.4
2,6-dimethyl-4-heptanone			537			2-butanol	269	14	272	3.4	1.2
2-decanone	625	17	622	2.9	0.5	2-methyl-1-propanol	274	14	271	3.3	1.2
3-decanone	628	17	628	0.5	0.1	2-methyl-2-propanol	275	14	276	1.4	0.5

Table 3. Continued

	V_c(exp)		this work		
compds	$cm^3 \cdot mol^{-1}$	ref	predict	D	100δ
4-decanone	628	17	629	1.2	0.2
5-decanone	628	17	631	2.9	0.5
2-undecanone	692	17	686	6.1	0.9
3-undecanone	692	17	691	0.6	0.1
4-undecanone	692	17	693	1.1	0.2
5-undecanone	692	17	695	2.8	0.4
6-undecanone	692	17	696	4.5	0.6
2-dodecanone	752	17	750	2.1	0.3
3-dodecanone	752	17	755	3.4	0.5
4-dodecanone	759	17	757	1.9	0.2
2-hexanol	384	14	391	6.9	1.8
3-hexanol	383	14	383	0.1	0.0
2-methyl-1-pentanol			377		
4-methyl-1-pentanol			379		
2-methyl-2-pentanol			383		
2-methyl-3-pentanol			365		
4-methyl-2-pentanol			377		
3-methyl-3-pentanol			437		
1-heptanol	435	14	455	19.8	4.6
2-heptanol	442	14	452	10.2	2.3
3-heptanol	434	14	444	10.5	2.4
4-heptanol	432	14	449	16.8	3.9
1-octanol	497	14	517	19.9	4.0
2-octanol	519	14	514	4.7	0.9
3-octanol	515	14	507	8.5	1.6
4-octanol	515	14	511	4.1	0.8
2-ethyl-1-hexanol			488		
1-nonanol	572	14	580	7.5	1.3
2-nonanol	575	14	577	1.9	0.3
3-nonanol	577	14	569	7.9	1.4
4-nonanol	575	14	586	10.6	1.8
1-decanol	649	14	642	6.5	1.0
2-decanol	646	14	640	6.1	0.9
3-decanol	643	14	632	10.9	1.7
4-decanol	643	14	636	6.5	1.0
5-decanol	646	14	641	5.1	0.8
1-undecanol	718	14	706	12.2	1.7
1-dodecanol			769		
phenol			175		
o-cresol			291		
m-cresol			320		
p-cresol			349		
2,3-xylenol			432		
2,4-xylenol			475		
2,5-xylenol			492		
2,6-xylenol			533		
3,4-xylenol			490		
3,5-xylenol			533		
3-ethylphenol			360		
2-ethylphenol			331		
ethy lamine	180	19	185	5.4	3.0
propylamine			236		
isopropylamine	219	19	240	20.9	9.5
trimethylamine	257	19	257	0.0	0.0
butylamine			292		
isobutylamine			282		
sec-butylamine			284		
tert-butylamine	293	19	293	0.0	0.0
diethylamine	304	19	300	4.1	1.4
pentylamine			350		
cyclopentylamine			290		
hexylamine			411		
1-octanamine	517	19	535	17.9	3.5
butyl ethylamine			453		
isopropyl propylamine			431		
triethylamine	389	19	389	0.0	0.0
dipropylamine			402		
diisopropylamine			421		
cyclohexylamine			360		
dibutylamine			516		
1,2-ethanediamine			221		
1,3-propanediamine			275		
1,4-butanediamine			333		
1,6-hexanediamine			453		
1,8-octanediamine			577		
1-pentanol	326	14	333	7.3	2.3
2-pentanol	329	14	331	1.7	0.5
3-pentanol	325	14	323	2.0	0.6
2-methyl-1-butanol			317		
3-methyl-1-butanol			324		
2-methyl-2-butanol			323		
3-methyl-2-butanol			321		
1,2-butanedial			284		
1,3-butanedial			300		
1-hexanol	387	14	394	6.5	1.7
4-ethylphenol			389		
diethyl ether	281	17	279	1.9	0.7
isopropyl methyl ether			295		
ethyl *n*-propyl ether	339	17	328	11.2	3.3
butyl methyl ether	329	17	338	9.4	2.8
methyl pentyl ether	391	17	392	0.6	0.1
butyl ethyl ether			381		
dipropyl ether			381		
diisopropyl ether	386	17	391	5.3	1.4
methyl formiate	172	17	179	6.9	4.0
methyl acetate	228	17	225	3.4	1.5
ethyl formiate	229	17	249	19.6	8.6
propyl formiate	285	17	286	0.5	0.2
n-pentyl methanoate	412	17	383	29.5	7.2
ethyl acetate	286	17	295	9.0	3.2
methyl propionate	282	17	285	3.3	1.2
propyl acetate	345	17	340	5.5	1.6
isopropyl acetate	344	17	344	0.0	0.0
methyl butanoate	340	17	336	4.3	1.3
methyl isobutanoate	339	17	358	19.0	5.6
2-propenyl acetate			219		
2-ethenyl acetate			154		
ethyl propionate	342	17	355	12.5	3.7
butyl acetate			390		
pentyl ethanoate	470	17	443	26.7	5.7
propyl propionate			403		
ethyl butanoate	415	17	405	10.0	2.4
n-propyl butyrate			458		
ethyl isobutanoate	415	17	421	5.9	1.4
methyl pentanoate	422	17	391	31.5	7.5
ethyl pentanoate			459		
propyl pentanoate			515		
isobutyl acetate	401	17	395	5.5	1.4
1-methylpropyl ethanoate			382		
isobutyl acrylate			433		
isobutyl butyrate			519		
isobutyl formate	355	17	337	17.8	5.0
diphenyl ether			503		
methylamine			125		
dimethylamine			180		
3,5-dimethylpyridine	357	19	357	0.2	0.1
propanenitrile	246	19	246	0.0	0.0
butanenitrile			295		
2-methylpropanenitrile			146		
pentanenitrile			352		
3-methylbutanenitrile			331		
2,2-dimethylpropanenitrile			167		
hexanenitrile			412		
octanenitrile			536		
decanenitrile			663		
chloroethane			212		
1-chloropropane	264	20	256	7.8	2.9
2-chloropropane	242	20	257	15.0	6.2
1-chlorobutane			308		
2-chlorobutane			297		
2-chloro-2-methylpropane			195		
1-chloropentane			364		
2-chloropentane			353		
1-chlorohexane			423		
1-chloroheptane			483		
1-chloro-3-methylbutane			372		
1,1-dichloroethane			236		
bromoethane	214	20	214	0.0	0.0
1-bromopropane			266		
2-bromopropane			266		

Table 3. Continued

compds	V_c(exp) $cm^3\cdot mol^{-1}$	ref	this work predict	this work D	this work 100δ
1,9-nonanediamine			640		
1,10-decanediamine			703		
1,12-dodecanediamine			830		
benzenamine	291	19	291	0.0	0.0
2-methylbenzenamine	346	19	346	0.0	0.0
3-nethylbenzenamine			375		
pyridine	247	19	245	1.8	0.7
2-methylpyridine	300	19	301	1.3	0.4
3-methylpyridine	300	19	301	1.3	0.4
4-methylpyridine	300	19	301	1.0	0.3
2,3-dimethylpyridine	357	19	357	0.2	0.1
2,4-dimethylpyridine	357	19	356	0.5	0.1
2,5-dimethylpyridine	357	19	357	0.2	0.1
2,6-dimethylpyridine	357	19	357	0.2	0.1
3,4-dimethylpyridine	357	19	356	0.5	0.1
1,2-dibromopropane			371		
1,1,2-trichloroethane			199		
methylthio methane	147	18	147	0.0	0.0
ethanethiol	207	18	220	13.0	6.3
1-propanethiol	286	18	261	25.3	8.9
2-propanethiol			271		
1-butanethiol	324	18	311	13.4	4.1
2-butanethiol			309		
2-methyl-1-propanethiol	307	21	306	0.7	0.2
2-methyl-2-propanethiol	307	21	309	2.3	0.6
1-pentanethiol			365		
2-methyl-1-butanethiol			349		
3-methyl-1-butanethiol			345		
2-methyl-2-butanethiol			357		
3-methyl-2-butanethiol			354		
2,2-dimethyl-1-propanethiol			342		
cyclopentanethiol			312		
1-hexanethiol			423		
1-bromobutane			325		
1-bromo-2-methylpropane			320		
2-bromo-2-methylpropane			145		
1-bromopentane			386		
methylthio ethane			187		
1-methylthio propane			247		
2-methylthio propane			257		
1-methylthio butane			308		
2-methyl-2-methylthio propane			307		
1-ethylthio propane			296		
2-ethylthio propane			307		
1-ethylthio butane			383		
2-ethylthio butane			376		
2-ethylthio-2-methyl propane			357		
methylthio cyclopentane			317		
2-methyl-2-pentanethiol			415		
2,3-dimethyl-2-butanethiol			405		
cyclohexanethiol	401	18	382	19.0	4.7
1-heptanethiol			482		
1-octanethiol	504		542	38.5	7.6
acetic acid	171	17	159	11.6	6.8
n-propanoic acid	233	17	225	7.9	3.4
acrylic acid			312		
n-butyric acid	292	17	277	15.3	5.2
n-pentanoic acid	346	17	333	13.5	3.9
2-ethyl butyric acid			380		
2-ethyl hexanoic acid	528	17	499	28.9	5.5
n-hexanoic acid	413	17	391	22.2	5.4
n-heptanoic acid	468	17	451	17.3	3.7
n-octanoic acid	519	17	512	7.4	1.4
n-nonanoic acid			573		
n-decanoic acid	638	17	635	2.6	0.4

[a] D is the absolute difference. $D = |V_{c,exp} - V_{c,pred}|$.

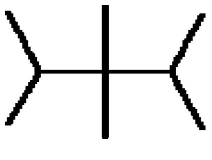
Conclusion

On the basis of the position group contribution method, a new method recently proposed for the estimation of the critical temperature and pressure is extended to the prediction of critical volume. Contributions for compounds containing carbon, hydrogen, oxygen, nitrogen, chlorine, and sulfur were reported, and that position distribution function has been developed which could distinguish between the thermodynamic properties of most isomers of organic compounds including *cis*- and *trans*- or *Z*- and *E*-structures. The results indicate that our model provides very satisfactory results, and the deviation from the most reliable experimental data is not more than 2.1 %. The overall average absolute difference for critical volume V_c predictions of 219 organic compounds is 8.8 $cm^3\cdot mol^{-1}$, and 2.1 % is the relative derivation. The higher prediction accuracy of the proposed method shown in our previous works and this work suggests that it is possible to use a similar framework to predict the three critical properties, T_c, P_c, and V_c of organic compounds containing various functionalities.

Appendix

Example 1.

Estimation of the critical volume of 2,3,3,4-tetramethylpentane



This compound is decomposed in position groups as follows: 4C−(CH)$(H)_3$; 2C−(C)$(H)_3$; 2C−$(C)_3$(H); 1C−$(C)_4$.

Total number of groups: $N = 9$.

The position factor: position of (CH) group 2, 4; the position correlation factor is $P = 2 + 4 = 6$.

Position of (C) group 3; the position correlation factor is $P = 3$.

Molecular weight: $M = 128.2551$.

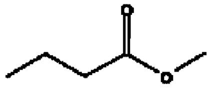
From the contributions in Table 1, the critical volume is estimated by eq 1

$$V_C/cm^3\cdot mol^{-1} = 44.253\cdot 4 + 39.01\cdot 2 + 78.892\cdot 2 + 102.7\cdot 1 - 5.06\cdot 6 - 8.151\cdot 3 + 46.24\cdot \exp(1/9) + 989.257\cdot \exp(1/128.2551) - 1011.117 = 498.3$$

The calculated result is 498.3 $cm^3\cdot mol^{-1}$, while the experimental critical volume is 498 $cm^3\cdot mol^{-1}$.

Example 2.

Estimation of the critical volume of Methyl butanoate



This compound is decomposed in position groups as follows: 1C−$(CH_2)(H)_3$; 1C−$(C)_2(H)_2$; 1 C−(C)(CO)$(H)_2$. 1CO−(CH2)(O); 1 O−(CO)(CH3); 1C−(O)$(H)_3$.

Total number of groups: $N = 6$.

The position of the (CO) group: the position correlation factor is $P = 4$.

Molecular weight: $M = 102.1317$.

From the contributions in Table 1, the critical volume is estimated by eq 1

$$V_C/cm^3\cdot mol^{-1} = 32.124\cdot 1 + 64.715\cdot 1 + 100.338\cdot 1 + 24.628 + 170.243\cdot \tanh(1/6) + 221.203\cdot \tanh(1/6) + +1.684\cdot 4 + 46.24\cdot \exp(1/6) + 989.257\cdot \exp(1/102.1317) - 1011.117 = 335.6$$

Therefore, the calculated result is 335.6 $cm^3\cdot mol^{-1}$, while the experimental critical volume is 336 $cm^3\cdot mol^{-1}$.

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