Position Group Contribution Method for the Prediction of the Critical Compressibility Factor of Organic Compounds

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On the basis of the group contribution and position distribution function, a simple and accurate model to predict the critical compressibility factor, Z_c, of organic compounds is presented in this study. The proposed model is developed to estimate Z_c of a variety of pure organic compounds involving a carbon chain from C_2 to C_{18}. Comparison results between experimental and calculated data indicate that our model provides very satisfactory results. The overall average absolute errors for Z_c predictions of 167 organic compounds is 0.007 with 2.45 % mean absolute relative derivation, which is compared to 0.018 and 6.90 % with the method of Joback and Reid, 0.016 and 5.94 % with the method of Constantinou and Gani, 0.012 and 4.73 % with the method of Wang et al., and 0.010 and 3.83 % with the method of Lee−Kesler. Also good prediction 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 critical properties, not only T_c, P_c, and V_c, but also Z_c, of organic compounds containing various functional groups, which further demonstrates the universality of our proposed method.

Introduction

Critical properties are especially essential parameters in many calculations involving phase equilibria and thermal properties, among which the critical compressibility factor, Z_c, of organic compounds is important, in particular, to reservoir and production engineers. Also Z_c is a critical parameter in some equations of state (EOS), such as the ER (Esmaeilzadeh−Roshanfekr) equation of state and the mER equation of state with special attention to application for reservoir fluids, and where the parameter Z_c is treated as an empirical parameter and has been correlated with the acentric factor.[1,2] Peng−Robinson[3] proposed an equation of state, usually used to predict the phase behavior of petroleum fluids, that assumes a value of the critical compressibility factor for all substances, and as a result, the predicted values for saturated liquid density differ considerably from their experimental values. Consequently, exact, credible, and accordant Z_c data are greatly necessary for production engineers or for some calculations. Unfortunately, the world literature data are very limited because experiments for obtaining these data are relatively time-consuming and expensive, if possible. It is therefore vital that prediction methods be developed to obtain Z_c data which are capable of reasonably accurate predictions.

Generally, being a parameter of each compound, Z_c can be estimated from an EOS, such as the two-parameter EOS (van der Waals or Peng−Robinson EOS) and the three-parameter EOS. Also some researchers correlated Z_c to the acentric factor, and an example of such correlations, shown as eq 1, is given by Lee−Kesler.[4] Owing to the good estimation performance, the group contribution methods are widely recommended and used for the prediction of critical properties.[5] Moreover, many researchers have tried to improve group contribution methods. Constantinou and Gani[6] and Olsen and Nielsen[7] developed new methods which perform estimations at different levels to distinguish among structural isomers. Recently, Wang et al.[8–10] proposed a position group contribution method for the prediction of critical parameters (T_c, P_c, V_c) of organic compounds with a similar framework, and the proposed method performed well in both accuracy and generality.

$$Z_c = 0.2905 - 0.085\omega \tag{1}$$

Therefore, the purpose of this study was to determine whether our proposed position group contribution method could be used directly for Z_c estimation. For this purpose, 167 organic compounds from the literature were selected, and the accuracy of our method is compared to the experimental data.

Method Proposed in This Work

Experimental Data. The sources of experimental data were from a series of critical compilation reviews by the critical properties group of IUPAC I.2 on thermodynamics; the works were published in *J. Chem. Eng. Data* by Ambrose et al.,[11] Tsonopoulos et al.,[12,15,17] Gude et al.,[13] Daubert et al.,[14] Kudchadker et al.,[16] and Marsh et al.[18,19] When all the groups' contribution values were determined, the recommended 167 experimental data from the literature were used to validate and evaluate the performance of our new method. The acentric factor data were from the DIPPR Database.

Position Group Contributions for the Critical Compressibility Factor. The critical compressibility factor function is constructed by all groups' contributions as well as the position distribution factor. The position distribution factors were used to take into account longer distance interactions. The molecule structures were described according to the IUPAC nominating method, and thus, only P_k values could be obtained for the

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

group	A	group	A
$\mathrm{C-(CH_3)(H)_3}$	−0.02363	$\mathrm{O-(CO)(H)}$	−0.06317
$\mathrm{C-(CH_2)(H)_3}$	−0.02037	$\mathrm{C-(C)(Br)(H)_2}$	0.02461
$\mathrm{C-(CH)(H)_3}$	−0.01785	$\mathrm{C-(C)_2(Br)(H)}$	0.10130
$\mathrm{C-(C)(H)_3}$	−0.02473	$\mathrm{C-(C)_3(Br)}$	−0.06414
$\mathrm{C-(C)_2(H)_2}$	−0.00120	$\mathrm{C-(C)(Cl)(H)_2}$	0.00100
$\mathrm{C-(C)_3(H)}$	0.01970	$\mathrm{C-(C)_2(Cl)(H)}$	−0.00173
$\mathrm{C-(C)_4}$	0.05211	$\mathrm{C-(C)(Cl)_2(H)}$	0.03053
$\mathrm{Cd-(H)(O)}$	−0.13091	$\mathrm{C-(S)(H)_3}$	−0.03976
$\mathrm{Cd-(H)_2}$	−0.19957	$\mathrm{C-(C)(S)(H)_2}$	−0.06699
$\mathrm{Cd-(C)(H)}$	0.12097	$\mathrm{C-(C)_2(S)(H)}$	−0.04417
$\mathrm{C-(Cd)(C)(H)_2}$	0.00232	$\mathrm{C-(C)_3(S)}$	0.00295
$\mathrm{C-(Cd)(H)_3}$	−0.03405	$\mathrm{Cb-(N)}$	−0.07184
$\mathrm{Cd-(C)_2}$	0.36332	$\mathrm{C-(N)(H)_3}$	−0.03310
$\mathrm{C-(Cd)(C)_2(H)}$	0.03424	$\mathrm{C-(C)(N)(H)_2}$	−0.00204
$\mathrm{Cd-(Cd)(H)}$	0.21533	$\mathrm{C-(C)_2(N)(H)}$	0.02432
$\mathrm{C-(O)(H)_3}$	−0.00305	$\mathrm{C-(C)_3(N)}$	0.05985
$\mathrm{C-(CO)(H)_3}$	−0.03180	$\mathrm{C-(C)(CN)(H)_2}$	−0.02048
$\mathrm{C-(C)(CO)(H)_2}$	−0.00729	$\mathrm{N-(C)(H)_2}$	−0.07915
$\mathrm{C-(C)_2(CO)(H)}$	0.03574	$\mathrm{N-(C)_2(H)}$	0.08253
$\mathrm{C-(C)_3(CO)}$	0.06894	$\mathrm{N-(C)_3}$	0.27790
$\mathrm{C-(C)(O)(H)_2}$	0.01642	$\mathrm{N-(Cb)(H)_2}$	0.53868
$\mathrm{C-(C)_2(O)(H)}$	0.03125	$\mathrm{N_I-(Cb)_2}$	−0.04813
$\mathrm{C-(C)_3(O)}$	0.06357	$\mathrm{S-(C)(H)}$	0.26238
$\mathrm{CO-(CH_3)(O)}$	−0.14836	$\mathrm{S-(C)_2}$	−0.04443
$\mathrm{CO-(CH_2)(O)}$	−0.14048	ortho correction[b]	0.00787
$\mathrm{CO-(CH)(O)}$	−0.27747	meta correction[b]	0.00403
$\mathrm{CO-(O)(H)}$	−0.20381	cyclopentane correction	−0.02793
$\mathrm{CO-(C)(H)}$	−0.08425	cyclohexane correction	−0.03029
$\mathrm{CO-(C)_2}$	0.06974	C_{ob}[c]	0.00405
$\mathrm{CO-(Cd)(O)}$	−0.05522	C_{mb}[c]	0.00188
$\mathrm{Cb-(H)}$	−0.05490	C_{pb}[c]	0.00066
$\mathrm{Cb-(C)}$	0.17379	cyclopropane correction	−0.04710
$\mathrm{C-(Cb)(H)_3}$	−0.03351	cyclobutane correction	−0.03773
$\mathrm{C-(Cb)(C)(H)_2}$	−0.02157	−(CH)< position correction	−0.00160
$\mathrm{C-(Cb)(C)_2(H)}$	0.01136	>(C)< position correction	−0.00030
$\mathrm{C-(Cb)(C)_3}$	0.04363	double bond position correction	−0.01390
$\mathrm{Cb-(O)}$	0.12007	$\mathrm{O-(C)(H)}$	0.00357
$\mathrm{O-(Cb)(H)}$	−0.36829	*trans* or *cis* structure correction	−0.00070
$\mathrm{O-(C)(H)}$	−0.26308	hydroxyl position correction	−0.00106
$\mathrm{O-(C)_2}$	−0.21812	phenol position correction	0.00203
$\mathrm{O-(CO)(CH_3)}$	0.08178	$\exp(1/N)$	−0.08700
$\mathrm{O-(CO)(CH_2)}$	0.06678	$\exp(1/M)$	2.61829
$\mathrm{O-(CO)(CH)}$	0.06391	Z_o	−2.23712

[a] 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. The usual symbols are used to represent the elements in their normal valence state. Elements in other valence states are distinguished by using additional characters, and furthermore, different symbols represent multiply 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 by five Cb atoms and one N_I atom. *trans* or *cis* correction: *cis* structure correction is 1, and *trans* structure correction 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 positions ortho, meta, and para with respect to the N element, respectively.

relevant positional factor, which could distinguish all isomers including *cis* and *trans* or *Z* and *E* structures of organic compounds for their thermodynamics properties.

Here, the position distribution function for Z_c estimation is expressed as eqs 2 and 3, and these expressions are similar in framework to our previous methods used for the prediction of the critical properties T_c, P_c, and V_c of organic compounds containing various functionalities. The parameter A_i or A_j is the i or j group contribution, N_i is the number of each group in which a carbon element forms the center of the group in the molecular formula, N_j is the number of each group in which a non-carbon element forms the center, N is the total number of groups, P_k is the position factor, and a_1 and a_2 are parameters of the model. The set of contributions that allowed minimization of the residual estimation difference was then computed by regression. Z_o is −2.23712, and M is the molecular weight. 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 a carbon chain from C_2 to C_{18}.

$$Z_c = Z_o + \sum_i A_i N_i + \sum_j A_j \tanh(N_j/N) + \sum_k A_k N_k + a_1 \exp(1/M) + a_2 \exp(1/N) \qquad (2)$$

$$N = \sum_i N_i + \sum_j N_j \qquad (3)$$

Comparison of Z_c Predicted with Different Methods. According to the definition of the compressibility factor, the critical compressibility factor Z_c is defined from T_c, P_c, and V_c as shown in eq 4. Generally, the method to estimate Z_c is first to estimate T_c, P_c, and V_c through methods and then to calculate Z_c through its definition. Essentially this is an indirect prediction method.

$$Z_c = \frac{P_c V_c}{R T_c} \qquad (4)$$

In this work, to evaluate the performance of our new method, we confirm the difference not only between our new direct Z_c prediction and experimental Z_c, but also between our new direct Z_c prediction and the Z_c calculation using the indirect prediction methods of Joback and Reid, Constantinou and Gani, and Wang et al. Moreover, the performance of our new model has been compared with that of the other direct prediction method of Lee−Kesler.

Results and Discussion

Prediction of the Critical Compressibility Factor. The results of the reference compounds obtained using the new position group contribution method are presented in Table 3. To illustrate

Table 2. Comparison of Z_c Predicted with Different Methods for Various Classes of Organic Compounds[a]

		Joback		Constantinou		Lee−Kesler		Wang		this work	
chemical family	no. of samples	AAD	$100\bar{\delta}$	AAD	$100\bar{\delta}$	AAD	$100\bar{\delta}$	AAD	$100\bar{\delta}$	AAD	$100\bar{\delta}$
alkanes and cycloalkanes	54	0.012	4.60	0.015	5.71	0.005	2.00	0.010	3.85	0.004	1.45
alkenes	10	0.010	3.71	0.008	2.96	0.006	2.02	0.004	1.55	0.006	2.26
aromatics	8	0.002	0.58	0.003	1.12	0.004	1.34	0.008	2.96	0.005	1.84
ketones and aldehydes	18	0.011	4.19	0.010	3.85	0.012	4.57	0.009	3.37	0.008	3.15
alcohols	19	0.011	4.43	0.011	4.09	0.021	8.16	0.008	3.18	0.005	2.02
acids	9	0.013	5.45	0.013	5.51	0.024	10.22	0.013	5.61	0.011	4.39
esters and ether oxides	23	0.029	10.84	0.026	9.92	0.010	3.42	0.015	5.72	0.007	2.72
amines and pyridines	18	0.037	13.57	0.026	9.54	0.007	2.58	0.026	9.65	0.006	2.08
nitriles and alkanethiols	8	0.056	19.91	0.019	7.01	0.017	6.23	0.026	9.50	0.021	7.57
overall	167	0.018	6.90	0.016	5.94	0.010	3.83	0.012	4.73	0.007	2.45

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

Table 3. Fully Predictive Estimations of the Critical Compressibility Factor Z_c[a]

			this work		
compd	$Z_{c,exptl}$	ref	prediction	D	100δ
ethane	0.279	11	0.279	0.000	0.00
propane	0.277	11	0.278	0.001	0.32
butane	0.274	11	0.272	0.002	0.84
2-methylpropane	0.278	14	0.278	0.000	0.07
pentane	0.268	11	0.267	0.001	0.34
2-methylbutane	0.27	14	0.271	0.001	0.26
2,2-dimethylpropane	0.272	14	0.264	0.008	2.94
hexane	0.264	11	0.263	0.001	0.23
2-methylpentane	0.27	14	0.267	0.003	1.11
3-methylpentane	0.274	14	0.263	0.011	4.09
2,2-dimethybutane	0.279	14	0.265	0.014	5.13
2,3-dimethylbutane	0.279	14	0.269	0.010	3.62
heptane	0.261	11	0.260	0.001	0.27
2-methylhexane	0.262	14	0.264	0.002	0.73
3-methylhexane	0.256	14	0.260	0.004	1.48
3-ethylpentane	0.267	14	0.257	0.010	3.67
2,2-dimethylpentane	0.266	14	0.262	0.004	1.65
2,3-dimethylpentane	0.256	14	0.263	0.007	2.85
2,4-dimethylpentane	0.265	14	0.264	0.001	0.30
3,3-dimethylpentane	0.274	14	0.266	0.008	3.03
2,2,3-trimethylbutane	0.265	14	0.264	0.001	0.53
octane	0.259	11	0.258	0.001	0.54
2-methylheptane	0.262	14	0.261	0.001	0.31
3-methylheptane	0.253	14	0.257	0.004	1.62
4-methylheptane	0.259	14	0.256	0.004	1.35
3-ethylhexane	0.252	14	0.255	0.003	1.03
2,2-dimethylhexane	0.265	14	0.259	0.006	2.30
2,3-dimethylhexane	0.263	14	0.261	0.002	0.87
2,4-dimethylhexane	0.263	14	0.259	0.004	1.48
2,5-dimethylhexane	0.262	14	0.260	0.002	0.76
3,3-dimethylhexane	0.251	14	0.263	0.012	4.78
3,4-dimethylhexane	0.265	14	0.255	0.010	3.81
2-methyl-3-ethylpentane	0.253	14	0.258	0.005	2.02
3-methyl-3-ethylpentane	0.266	14	0.267	0.001	0.53
2,2,3-trimethylpentane	0.254	14	0.258	0.004	1.73
2,2,4-trimethylpentane	0.267	14	0.259	0.008	2.88
2,3,3-trimethylpentane	0.269	14	0.267	0.002	0.89
2,3,4-trimethylpentane	0.267	14	0.261	0.006	2.25
nonane	0.257	11	0.255	0.002	0.66
2-methyloctane			0.259		
2,2-dimethyloctane			0.257		
2,3-dimethyloctane			0.256		
2,4-dimethyloctane			0.255		
2,5-dimethyloctane			0.253		
2,6-dimethyloctane			0.251		
2,7-dimethyloctane			0.252		
3,3-dimethyloctane			0.259		
3,4-dimethyloctane			0.250		
3,5-dimethyloctane			0.249		
3,6-dimethyloctane			0.247		
4,4-dimethyloctane			0.258		
4,5-dimethyloctane			0.247		
4-propylheptane			0.248		
3-ethyl-2-methylheptane			0.254		
3-ethyl-3-methylheptane			0.263		
3-ethyl-4-methylheptane			0.248		
3-ethyl-5-methylheptane			0.246		
4-ethyl-2-methylheptane			0.252		
4-ethyl-3-methylheptane			0.248		
4-ethyl-4-methylheptane			0.269		
5-ethyl-2-methylheptane			0.250		
2,2,3-trimethylheptane			0.254		
2,2,4-trimethylheptane			0.252		
2,2,5-trimethylheptane			0.251		
2,2,6-trimethylheptane			0.252		
2,3,3-trimethylheptane			0.262		
2,3,4-trimethylheptane			0.254		
2,3,5-trimethylheptane			0.252		
2,3,6-trimethylheptane			0.253		
2,4,4-trimethylheptane			0.262		
2,4,5-trimethylheptane			0.251		
2,4,6-trimethylheptane			0.252		
2,5,5-trimethylheptane			0.261		
3,3,4-trimethylheptane			0.256		
3-methyloctane			0.255		
4-methyloctane			0.253		
2-ethylheptane			0.256		
3-ethylheptane			0.252		
4-ethylheptane			0.251		
2,2-dimethylheptane			0.257		
2,3-dimethylheptane			0.258		
2,4-dimethylheptane			0.257		
2,5-dimethylheptane			0.255		
2,6-dimethylheptane			0.256		
3,3-dimethylheptane			0.261		
3,4-dimethylheptane			0.253		
3,5-dimethylheptane			0.251		
4,4-dimethylheptane			0.260		
3-ethyl-2-metylhexane			0.256		
3-ethyl-3-metylhexane			0.265		
3-ethyl-4-metylhexane			0.250		
4-ethyl-2-metylhexane			0.254		
2,2,3-trimethylhexane			0.256		
2,2,4-trimethylhexane			0.254		
2,2,5-trimethylhexane			0.255		
2,3,3-trimethylhexane			0.264		
2,3,5-trimethylhexane			0.257		
2,4,4-trimethylhexane			0.264		
3,3,4-trimethylhexane			0.259		
3,3-diethylpentane			0.279		
3-ethyl-2,2-dimethylpentane			0.254		
3-ethyl-2,3-dimethylpentane			0.269		
3-ethyl-2,4-dimethylpentane			0.256		
2,2,3,3-tetramethylpentane			0.262		
2,2,3,4-tetramethylpentane			0.256		
2,2,4,4-tetramethylpentane			0.257		
2,3,3,4-tetramethylpentane			0.265		
decane	0.256	11	0.253	0.003	1.13
2-methylnonane			0.257		
3-methylnonane			0.253		
4-methylnonane			0.251		
5-methylnonane			0.249		
3-ethyloctane			0.250		
4-ethyloctane			0.248		
3-ethyl-2,3-dimethylhexane			0.264		
3-ethyl-2,4-dimethylhexane			0.252		
3-ethyl-2,5-dimethylhexane			0.252		
3-ethyl-3,4-dimethylhexane			0.261		
4-ethyl-2,2-dimethylhexane			0.250		
4-ethyl-2,4-dimethylhexane			0.266		
4-ethyl-3,3-dimethylhexane			0.254		
2,2,3,3-tetramethylhexane			0.260		
2,2,3,4-tetramethylhexane			0.252		
2,2,3,5-tetramethylhexane			0.253		
2,2,4,4-tetramethylhexane			0.260		
2,2,5,5-tetramethylhexane			0.255		
2,2,4,5-tetramethylhexane			0.251		
2,3,3,4-tetramethylhexane			0.260		
2,3,3,5-tetramethylhexane			0.261		
2,3,4,4-tetramethylhexane			0.261		
2,3,4,5-tetramethylhexane			0.253		
3,3,4,4-tetramethylhexane			0.264		
3,3-diethyl-2-methylpentane			0.267		
3-ethyl-2,2,3-trimethylpentane			0.271		
3-ethyl-2,2,4-trimethylpentane			0.252		
3-ethyl-2,3,4-trimethylpentane			0.267		
2,2,3,3,4-pentamethylpentane			0.258		
2,2,3,4,4-pentamethylpentane			0.255		
undecane	0.257	11	0.251	0.006	2.30
dodecane	0.251	11	0.249	0.002	0.72
tridecane	0.246	11	0.248	0.002	0.61
tetradecane	0.244	11	0.246	0.002	0.74
pentadecane	0.243	11	0.244	0.001	0.45
hexadecane	0.241	11	0.243	0.002	0.62
heptadecane	0.242	11	0.241	0.001	0.41
octadecane	0.247	11	0.240	0.007	2.83
cyclopropane	0.272	14	0.272	0.000	0.00
cyclobutane			0.274		

Table 3. Continued

			this work						this work		
compd	$Z_{c,exptl}$	ref	prediction	D	100δ	compd	$Z_{c,exptl}$	ref	prediction	D	100δ
3,3,5-trimethylheptane			0.255			cyclopentane	0.275	14	0.279	0.004	1.31
3,4,4-trimethylheptane			0.258			cyclohexane	0.273	14	0.272	0.001	0.29
3,4,5-trimethylheptane			0.252			methylcyclopentane	0.272	14	0.277	0.005	1.91
3,4-diethylhexane			0.245			methylcyclohexane	0.27	14	0.272	0.002	0.56
3,3-diethylhexane			0.267			ethylcyclopentane	0.269	14	0.271	0.002	0.89
3-ethyl-2,2-dimethylhexane			0.272			*cis*-1,2-dimethylcyclopentane			0.274		
trans-1,2-dimethylcyclopentane			0.276			*trans*-3-heptene			0.263		
cis-1,3-dimethylcyclopentane			0.273			1-octene	0.266	15	0.260	0.007	2.44
trans-1,3-dimethylcyclopentane			0.274			*cis*-2-octene			0.251		
1,1-dimethylcyclopentane			0.277			*trans*-2-octene			0.253		
1,1-dimethylcyclohexane			0.272			*cis*-3-octene			0.255		
cis-1,2-dimethylcyclohexane			0.269			*trans*-3-octene			0.256		
trans-1,2-dimethylcyclohexane			0.271			*cis*-4-octene			0.241		
cis-1,3-dimethylcyclohexane			0.268			*trans*-4-octene			0.242		
trans-1,3-dimethylcyclohexane			0.269			1-nonene			0.258		
cis-1,4-dimethylcyclohexane			0.266			1-decene	0.253	15	0.257	0.004	1.50
trans-1,4-dimethylcyclohexane			0.267			1-undecene			0.255		
ethylcyclohexane			0.266			1-dodecene			0.254		
propylcyclopentane			0.266			1,3-butadiene	0.27	15	0.270	0.000	0.00
propylcyclohexane			0.264			benzene	0.268	12	0.270	0.002	0.86
butylcyclopentane			0.266			methylbenzene	0.264	12	0.267	0.003	1.10
butylcyclohexane			0.262			1,4-dimethylbenzene	0.259	12	0.258	0.002	0.58
pentylcyclopentane			0.264			1,2-dimethylbenzene	0.263	12	0.265	0.002	0.91
pentylcyclohexane			0.260			1,3-dimethylbenzene	0.259	12	0.262	0.003	1.00
hexylcyclopentane			0.262			ethylbenzene	0.263	12	0.257	0.006	2.43
heptylcyclohexane			0.260			1,2,3-trimethylbenzene			0.263		
1-butene	0.278	15	0.265	0.012	4.40	1,2,4-trimethylbenzene			0.255		
cis-2-butene	0.272	15	0.276	0.004	1.40	1,3,5-trimethylbenzene			0.256		
trans-2-butene	0.274	15	0.277	0.004	1.35	1,2,3,4-tetramethylbenzene			0.257		
1-pentene	0.275	15	0.264	0.011	4.07	1,2,3,5-tetramethylbenzene			0.254		
trans-2-pentene			0.279			1,2,4,5-tetramethylbenzene			0.250		
2-methyl-1-butene			0.279			1-methyl-2-ethylbenzene			0.253		
2-methyl-2-butene			0.278			1-methyl-3-ethylbenzene			0.250		
3-methyl-1-butene	0.286	15	0.282	0.004	1.54	1-methyl-4-ethylbenzene			0.246		
1-hexene	0.272	15	0.262	0.010	3.57	propylbenzene	0.265	12	0.254	0.011	4.08
cis-2-hexene			0.267			isopropylbenzene			0.273		
trans-2-hexene			0.268			1-methyl-2-isopropylbenzene			0.268		
cis-3-hexene			0.270			1-methyl-3-isopropylbenzene			0.264		
trans-3-hexene			0.272			1-methyl-4-isopropylbenzene			0.260		
2-methyl-1-hexene			0.259			butylbenzene	0.262	12	0.252	0.010	3.74
3-methyl-1-hexene			0.271			*sec*-butylbenzene			0.269		
4-methyl-1-hexene			0.259			*tert*-butylbenzene			0.266		
1-heptene	0.267	15	0.261	0.006	2.28	pentylbenzene			0.251		
cis-2-heptene			0.258			hexylbenzene			0.249		
trans-2-heptene			0.260			heptylbenzene			0.247		
cis-3-heptene			0.262			butanone	0.252	16	0.262	0.010	3.81
2-pentanone	0.253	16	0.257	0.004	1.38	5-tridecanone			0.236		
3-pentanone	0.264	16	0.261	0.003	1.21	6-tridecanone			0.235		
3-methyl-2-butanone	0.255	16	0.281	0.026	10.04	7-tridecanone			0.234		
2-hexanone	0.255	16	0.252	0.003	1.14	2-tetradecanone			0.231		
3-hexanone	0.259	16	0.256	0.003	1.00	3-tetradecanone			0.236		
3,3-dimethyl-2-butanone	0.276	16	0.276	0.000	0.00	4-tetradecanone			0.235		
4-methyl-2-pentanone			0.249			7-tetradecanone			0.232		
2-heptanone	0.256	16	0.249	0.008	2.93	1-propanal	0.256	16	0.249	0.007	2.58
3-heptanone			0.253			1-butanal	0.25	16	0.256	0.006	2.20
4-heptanone			0.252			1-pentanal	0.264	16	0.258	0.006	2.39
2-octanone			0.245			1-hexanal	0.266	16	0.258	0.008	2.86
3-octanone			0.250			1-heptanal	0.267	16	0.258	0.009	3.22
4-octanone			0.249			1-octanal	0.272	16	0.258	0.014	5.18
2-methyl-3-hexanone			0.279			1-nonanal	0.266	16	0.257	0.009	3.31
5-methyl-2-hexanone			0.247			1-decanal	0.278	16	0.256	0.022	7.81
2,4-dimethyl-3-pentanone			0.301			2-methylpropanal			0.281		
2-methyl-3-heptanone			0.309			2-methylhexanal			0.262		
5-methyl-3-heptanone			0.245			3-methylhexanal			0.258		
2,5-dimethyl-3-hexanone			0.274			ethanol	0.241	13	0.232	0.009	3.65
5-nonanone	0.244	16	0.245	0.001	0.29	1-propanol	0.252	13	0.247	0.005	1.83
4-nonanone			0.246			2-propanol	0.25	13	0.252	0.002	0.64
3-nonanone			0.247			1-butanol	0.258	13	0.256	0.002	0.89
2-nonanone	0.256	16	0.243	0.014	5.27	2-butanol	0.253	13	0.258	0.005	1.78
2-decanone			0.240			2-methyl-1-propanol	0.258	13	0.259	0.001	0.50
3-decanone			0.244			2-methyl-2-propanol	0.259	13	0.273	0.014	5.21
4-decanone			0.243			1-pentanol	0.26	13	0.261	0.001	0.31
5-decanone			0.242			2-pentanol	0.259	13	0.263	0.004	1.39
2-undecanone			0.238			3-pentanol			0.264		

Table 3. Continued

			this work		
compd	$Z_{c,exptl}$	ref	prediction	D	100δ
3-undecanone			0.242		
4-undecanone			0.241		
5-undecanone			0.240		
6-undecanone			0.239		
2-dodecanone			0.235		
3-dodecanone			0.240		
4-dodecanone			0.239		
5-dodecanone			0.238		
6-dodecanone			0.237		
2-tridecanone			0.233		
3-tridecanone			0.238		
4-tridecanone			0.237		
2-methyl-3-pentanol			0.250		
4-methyl-2-pentanol			0.266		
3 methyl 3 pentanol			0.308		
1-heptanol	0.253	13	0.266	0.013	5.18
2-heptanol	0.264	13	0.268	0.004	1.44
3-heptanol			0.269		
4-heptanol			0.273		
1-octanol	0.254	13	0.267	0.013	5.28
2-octanol	0.273	13	0.269	0.004	1.39
3-octanol			0.270		
4-octanol			0.274		
2-ethyl-1-hexanol			0.266		
1-nonanol	0.26	13	0.268	0.008	3.15
2-nonanol	0.269	13	0.270	0.001	0.37
3-nonanol			0.271		
4-nonanol			0.277		
1-decanol	0.263	13	0.269	0.006	2.13
2-decanol			0.270		
3-decanol			0.271		
4-decanol			0.275		
5-decanol			0.279		
1-undecanol			0.269		
1-dodecanol			0.269		
phenol			0.240		
o-cresol			0.243		
m-cresol			0.245		
p-cresol			0.247		
2,3-xylenol			0.249		
2,4-xylenol			0.248		
2,5-xylenol			0.246		
2,6-xylenol			0.252		
3,4-xylenol			0.253		
3,5-xylenol			0.252		
3-ethylphenol			0.239		
2-ethylphenol			0.236		
4-ethylphenol			0.241		
diethyl ether	0.264	16	0.260	0.005	1.70
ethyl *n*-propyl ether	0.275	16	0.263	0.012	4.33
butyl methyl ether	0.26	16	0.263	0.003	1.08
methyl pentyl ether	0.262	16	0.265	0.003	1.15
sec-butylamine			0.280		
tert-butylamine	0.281	18	0.281	0.000	0.00
diethylamine	0.275	18	0.282	0.007	2.69
pentylamine			0.270		
cyclopentylamine			0.288		
hexylamine			0.268		
1-octanamine	0.252	18	0.266	0.014	5.52
triethylamine	0.265	18	0.279	0.014	5.28
dipropylamine			0.271		
diisopropylamine			0.268		
cyclohexylamine			0.284		
dibutylamine			0.264		
1,2-ethanediamine			0.273		
1,3-propanediamine			0.275		
1,4-butanediamine			0.276		
1,6-hexanediamine			0.277		
1,8-octanediamine			0.276		
1,9-nonanediamine			0.276		
1,10-decanediamine			0.275		
1,12-dodecanediamine			0.274		
benzenamine	0.28	18	0.280	0.000	0.00
2-methylbenzenamine	0.273	18	0.269	0.004	1.43
2-methyl-1-butanol			0.262		
3-methyl-1-butanol			0.263		
2-methyl-2-butanol			0.275		
3-methyl-2-butanol			0.265		
1,2-butanediol			0.260		
1,3-butanediol			0.266		
1-hexanol	0.261	13	0.264	0.003	1.15
2-hexanol	0.261	13	0.266	0.005	1.84
3-hexanol	0.266	13	0.267	0.001	0.30
2-methyl-1-pentanol			0.265		
4-methyl-1-pentanol			0.264		
2-methyl-2-pentanol			0.278		
butyl ethyl ether			0.265		
dipropyl ether			0.265		
diisopropyl ether	0.263	16	0.267	0.004	1.41
methyl formiate	0.255	16	0.260	0.005	2.12
methyl acetate	0.257	16	0.252	0.005	2.02
ethyl formiate	0.257	16	0.267	0.010	3.70
propyl formiate	0.259	16	0.272	0.013	4.83
pentyl formiate	0.298	16	0.275	0.023	7.58
ethyl acetate	0.255	16	0.251	0.004	1.65
methyl propionate	0.256	16	0.259	0.003	1.29
propyl acetate	0.254	16	0.252	0.002	0.94
isopropyl acetate	0.258	16	0.252	0.006	2.40
methyl butanoate	0.256	16	0.258	0.002	0.90
methyl isobutanoate	0.259	16	0.266	0.007	2.55
2-propenyl acetate			0.203		
2-ethenyl acetate			0.149		
ethyl propionate	0.26	16	0.257	0.003	1.08
butyl acetate			0.252		
pentyl ethanoate	0.258	16	0.251	0.007	2.67
propyl propionate			0.257		
ethyl butanoate	0.263	16	0.256	0.007	2.70
propyl pentanoate			0.255		
ethyl isobutanoate	0.279	16	0.286	0.007	2.47
methyl pentanoate	0.275	16	0.257	0.018	6.65
ethyl pentanoate			0.254		
propyl pentanoate			0.254		
isobutyl acetate	0.257	16	0.258	0.001	0.54
methylpropyl ethanoate			0.249		
isobutyl acrylate			0.262		
isobutyl butyrate			0.261		
isobutyl formate	0.301	16	0.281	0.020	6.68
diphenyl ether			0.256		
methylamine			0.254		
dimethylamine			0.279		
ethylamine	0.266	18	0.271	0.005	1.73
propylamine			0.271		
isopropylamine	0.254	18	0.283	0.029	11.57
trimethylamine	0.291	18	0.283	0.008	2.78
butylamine			0.271		
isobutylamine			0.273		
chloroethane			0.259		
1-chloropropane	0.289	19	0.273	0.016	5.64
2-chloropropane	0.257	19	0.256	0.001	0.43
1-chlorobutane			0.276		
2-chlorobutane			0.257		
2-chloro-2-methylpropane			0.224		
1-chloropentane			0.277		
2-chloropentane			0.257		
1-chlorohexane			0.276		
1-chloroheptane			0.275		
1-chloro-3-methylbutane			0.279		
1,1-dichloroethane			0.277		
bromoethane	0.296	19	0.266	0.030	10.10
1-bromopropane			0.284		
2-bromopropane			0.339		
1-bromobutane			0.291		
1-bromo-2-methylpropane			0.294		
2-bromo-2-methylpropane			0.150		
1-bromopentane			0.293		
(methylthio)ethane			0.166		
1-(methylthio)propane			0.167		
2-(methylthio)propane			0.176		

Table 3. Continued

compd	$Z_{c,exptl}$	ref	this work		
			prediction	D	100δ
3-methylbenzenamine			0.271		
pyridine	0.271	18	0.266	0.005	1.73
2-methylpyridine	0.269	18	0.269	0.000	0.04
3-methylpyridine	0.262	18	0.267	0.005	1.87
4-methylpyridine	0.261	18	0.266	0.005	1.80
2,3-dimethylpyridine	0.269	18	0.263	0.006	2.23
2,4-dimethylpyridine	0.262	18	0.262	0.000	0.11
2,5-dimethylpyridine	0.257	18	0.263	0.006	2.33
2,6-dimethylpyridine	0.265	18	0.265	0.000	0.04
3,4-dimethylpyridine	0.264	18	0.260	0.004	1.67
3,5-dimethylpyridine	0.261	18	0.261	0.000	0.08
propanenitrile	0.225	18	0.245	0.020	8.80
butanenitrile			0.256		
pentanenitrile			0.258		
3-methylbutanenitrile			0.257		
hexanenitrile			0.258		
octanenitrile			0.255		
decanenitrile			0.252		
3-methyl-1-butanethiol			0.244		
2-methyl-2-butanethiol			0.279		
3-methyl-2-butanethiol			0.264		
2,2-dimethyl-1-propanethiol			0.257		
cyclopentanethiol			0.271		
1-hexanethiol			0.248		
2-methyl-2-pentanethiol			0.271		
2,3-dimethyl-2-butanethiol			0.273		
cyclohexanethiol			0.260		
1-heptanethiol			0.242		
1-octanethiol			0.236		
1-(methylthio)butane			0.167		
2-methyl-2-(methylthio)propane			0.185		
1-(ethylthio)propane			0.120		
2-(ethylthio)propane			0.129		
1-(ethylthio)butane			0.125		
2-(ethylthio)butane			0.124		
2-(ethylthio)-2-methyl propane			0.138		
(methylthio)cyclopentane			0.181		
(methylthio)methane	0.272	17	0.221	0.051	18.79
ethanethiol	0.274	17	0.299	0.025	9.20
1-propanethiol	0.295	17	0.280	0.015	5.15
2-propanethiol			0.288		
1-butanethiol	0.273	17	0.266	0.007	2.53
2-butanethiol			0.272		
2-methyl-1-propanethiol			0.270		
2-methyl-2-propanethiol			0.285		
1-pentanethiol			0.256		
2-methyl-1-butanethiol			0.257		
acetic acid	0.201	16	0.204	0.003	1.44
propanoic acid	0.219	16	0.228	0.009	3.88
acrylic acid			0.230		
butyric acid	0.232	16	0.236	0.004	1.59
pentanoic acid	0.237	16	0.241	0.004	1.48
2-ethyl butyric acid			0.245		
2-ethyl hexanoic acid	0.262	16	0.251	0.011	4.05
hexanoic acid	0.256	16	0.243	0.013	4.96
heptanoic acid	0.262	16	0.245	0.017	6.49
octanoic acid	0.259	16	0.246	0.013	5.06
decanoic acid	0.223	16	0.247	0.024	10.58

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

the application of the proposed method, a detailed procedure for the estimation of critical properties is given in the Appendix for Z_c. Table 2 compares Z_c 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.

$$\mathrm{AAD} = \frac{\sum |Z_{c,exptl} - Z_{c,pred}|}{n} \tag{5}$$

$$\delta = \left|\frac{Z_{c,exptl} - Z_{c,pred}}{Z_{c,exptl}}\right| \tag{6}$$

$$\bar{\delta} = \frac{1}{N}\sum_{n}\left|\frac{Z_{c,exptl} - Z_{c,pred}}{Z_{c,exptl}}\right| \tag{7}$$

The performance of the new model has been compared with that of other estimation methods from the literature, and the results indicate that the new model is significantly more reliable. The results presented in Table 2 show that the proposed method is more accurate than other methods for Z_c prediction. AAD for Z_c prediction of 167 organic compounds is 0.007 and $\bar{\delta}$ is 2.45 %, which are compared to 0.018 and 6.90 % with the method of Joback and Reid, 0.016 and 5.94 % with the method of Constantinou and Gani, 0.012 and 4.73 % with the method of Wang et al., and 0.010 and 3.83 % with the method of Lee−Kesler.

According to Wang et al.'s previous work,[8–10] $\bar{\delta}$ for T_c, P_c, and V_c was 1.1 %, 2.4 %, and 2.1 %, respectively, and if the Z_c calculation was obtained through the prediction results of T_c, P_c, and V_c, $\bar{\delta}$ would be 4.73 %. This is because both T_c, P_c, and V_c prediction and Z_c prediction could contribute to the overall errors. Consequencely, even though T_c, P_c, and V_c prediction methods are much more precise than other methods, they are likely to increase Z_c prediction errors on the basis of the prediction results of T_c, P_c, and V_c. Similarly, the accumulative total error might be even greater for Joback and Reid's method and Constantinou and Gani's method. Therfore, from this work, it can be demonstrated that the indirect method for Z_c prediction, based on the prediction results of T_c, P_c, and V_c, should not be recommended because of the accumulative total errors, and our direct Z_c prediction method is more precise than Lee−Kesler's method.

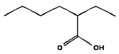
The results presented in Table 3 prove that the predicted Z_c values agree well with the experimental results, which indicates that our new position group contribution method for predicting Z_c has good overall accuracy. Also, the results presented in Table 3 show that our new simple model gives low deviations and can be used with confidence in thermodynamic and engineering calculations.

Conclusion

The objective of this work was to develop and evaluate our new position group contribution method for predicting the critical compressibility factor, Z_c. For this purpose, 167 organic compounds from the literature were selected. In this paper, contributions for compounds containing carbon, hydrogen, oxygen, nitrogen, chlorine, and sulfur are reported, and a position distribution function is developed which could distinguish between the thermodynamic properties of all isomers of organic compounds including *cis* and *trans* or *Z* and *E* structures. The accuracy of our method is compared to the experimental data, and the results indicate that our model provides very satisfactory results. The overall average absolute difference and the relative derivation for Z_c predictions of 167 organic compounds are found to be 0.007 and 2.45 %, respectively. Also, it is proven that our model performs significantly better than those proposed by Joback and Reid, Constantinou and Gani, Wang et al., and Lee−Kesler. Moreover, from this work, it can be demonstrated that the indirect method for Z_c prediction, based on the prediction results of T_c, P_c, and V_c, should not be recommended because of the accumulative total errors. More importantly, 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 critical properties, not only T_c, P_c, and V_c, but also Z_c, of organic compounds containing various functionalities.

Appendix

Example 1. Estimation of Z_c of 2-Ethylhexanoic Acid.

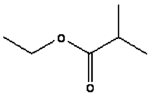


This compound is decomposed in position groups as follows: two $C-(CH_2)(H)_3$ groups, four $C-(C)_2(H)_2$ groups, one $C-(C)_2(CO)(H)$ group, one $CO-(CH)(O)$ group, one $O-(CO)(H)$ group. The total number of groups $N = 9$. The position factor for the position of (CH) group 2 is $P = 2$. The molecular weight $M = 144.214$. From the contributions in Table 1, Z_c is estimated by eq 1:

$$Z_c = -2.23712 - 0.02037\cdot 2 - 0.00120\cdot 4 + 0.03574 - 0.27747\tanh(1/9) - 0.06317\tanh(1/9) - 0.00160\cdot 2 - 0.087\exp(1/9) + 2.61929\exp(1/144.214) = 0.252$$

The calculated result is 0.252 while the experimental Z_c is 0.262.

Example 2. Estimation of Z_c of Ethyl Isobutanoate.



This compound is decomposed in position groups as follows: one $C-(CH_2)(H)_3$ group, two $C-(CH)(H)_3$ groups, one $C-(C)_2(CO)(H)$ group, one $C-(C)(O)(H)_2$ group, one $CO-(CH)(O)$ group, and $O-(CO)(CH_2)$ group. The total number of groups $N = 7$. The position factor for the position of the (CO) group is $P = 3$. The molecular weight $M = 116.16$. From the contributions in Table 1, Z_c is estimated by eq 1:

$$Z_c = -2.23712 - 0.02037 - 0.01785\cdot 2 + 0.03574 + 0.01642 - 0.14048\tanh(1/7) + 0.06678\tanh(1/7) - 0.00106\cdot 3 - 0.087\exp(1/7) + 2.61929\exp(1/116.16) = 0.286$$

Therefore, the calculated result is 0.286, while the experimental Z_c is 0.279.

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