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

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A new group contribution method based on position group contribution additivity is developed and applied for the prediction of critical pressure P_c of pure organic compounds involving the carbon chain from C2 to C18. Contributions for organic compounds containing oxygen, nitrogen, chlorine, bromine, and sulfur are given. Also, the proposed method is compared against other predictive methods. The overall average absolute errors for critical pressure P_c predictions of 232 organic compounds is 0.08 MPa and 2.4 % mean absolute relative derivation, which is compared to 0.19 MPa and 5.1 % with the method of Joback, and 0.21 MPa and 5.4 % with the method of Constantinou and Gani. Owing to the utilization of the position correlation factor, the proposed method outperforms the other alternatives both in accuracy and generality, especially in the capability of distinguishing between isomers. Moreover, critical pressure P_c can be estimated from the chemical structure alone, which demonstrates that this new position contribution group method is fully predictive.

Introduction

The increasing use of high pressure in chemical technology calls for the knowledge of fluid phase behavior in the critical region. Hence, critical property data are of great practical importance as they are the basis for many industrial process designs. However, the world literature experimental critical data resources are really poor, and the accuracy of some of these quite older values is even questionable. Unfortunately, most components are not sufficiently stable at or near the critical temperature, and as a result, experimental measurements of their critical properties, T_c and P_c, are extremely difficult, if not impossible. It is therefore vital that prediction methods be developed to obtain critical property values which are reliable. Group contribution methods have been widely used to predict many thermodynamic properties. However, most of the 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.

On the basis of the first-order group techniques,[1–3] Jalowka−Karbert,[4] Constantinou−Gani,[5] and Marrero−Gani[6,7] developed second-order group techniques, which additionally take into consideration the influence of first- and second-nearest neighbors of a considered group. Nannoolal et al.[8] recently developed an equation for the prediction of critical pressure.

In this study, a new estimation method is developed based on our experience with previous work on the critical temperature.[9] As our preliminary work 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 pressure. This study will be followed by the next one, dealing with critical volumes of hydrocarbons, as well as with evaluation and employing new predictive methods.

Method Proposed in This Work

Experimental Data. The quality of a method strongly depends on the amount and quality of the experimental data used in its development. A total of 232 compounds were used for the determination of group contributions, which includes linear and branched alkanes and cycloalkanes (62), alkenes (12), aromatics (13), ketones and aldehydes (20), alcohols (29), acids (9), phenols and ether oxides (11), esters (23), amines (25), nitriles (5), pyridines (10), and chlorobromoalkanes and thiols (13).

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 the *Journal of Chemical and Engineering Data* by Ambrose,[10–12] Tsonopoulous,[11,12,15,17] Daubert,[14] Gude,[13] Kudchadker,[16] and Marsh et al.[18,19] Critical data were also obtained from a compilation of organic property data by Ma.[20]

Position Group Contributions for the Critical Pressure. The first step consisted of testing correlations to represent the properties. Only a one-parameter contribution was considered for each group. The critical pressure function is constructed by all groups' contributions as well as position correction. The position corrections were used to take into account longer distance interactions, which could distinguish most isomer, including *cis*- and *trans*- or *Z*- and *E*-, structures of organic compounds for their thermodynamic properties.

Here, the critical pressure is expressed as

$$P_C = P_0 + \sum_i A_i N_i + \sum_j A_j \tanh(N_j/N) + \sum_k A_k P_k + a_1 \exp(1/M) + a_2 \exp(1/N) \quad (1)$$

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$$N = \sum_i N_i + \sum_j N_j \tag{2}$$

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 total number of groups, P_k for position correlation factor, and a_1, a_2 for parameters of the model. The set of contributions that allowed us to minimize the residual estimation difference was then computed by regression. P_0 is −124.843 MPa, and M is 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 carbon chain from C2 to C18.

Results and Discussion

Prediction of Critical Pressure. 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 pressure. Table 2 compares the critical pressure predictions obtained using our method and previous methods to experimental data. Also, the overall average absolute difference (AD) 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.

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

group	A/MPa	group	A/MPa
C−(CH3)(H)3	−0.5425	C−(C)(Br)(H)2	−0.8532
C−(CH2)(H)3	−0.1151	C−(C)(Cl)(H)2	−0.5617
C−(CH)(H)3	−0.1406	C−(C)2(Cl)(H)	−0.6716
C−(C)(H)3	−0.2478	C−(C)(Cl)2(H)	−1.0226
C−(C)2(H)2	−0.0882	C−(C)(S)(H)2	−0.4868
C−(C)3(H)	−0.0596	C−(C)2(S)(H)	−0.3348
C−(C)4	0.2912	C−(C)3(S)	0.0123
Cd−(H)(O)	−2.6099	Cb−(N)	8.1548
Cd−(H)2	−0.3539	C−(N)(H)3	0.1178
Cd−(C)(H)	1.0576	C−(C)(N)(H)2	−0.5161
C−(Cd)(C)(H)2	−0.2146	C−(C)2(N)(H)	0.9004
C−(Cd)(H)3	−0.2787	C−(C)3(N)	0.7889
Cd−(C)2	1.4366	C−(C)(CN)(H)2	0.3345
C−(Cd)(C)2(H)	−0.1745	N−(CH3)(H)2	3.2138
Cd−(Cd)(H)	0.5441	N−(CH2)(H)2	6.9729
C−(O)(H)3	−0.2372	N−(CH)(H)2	0.6923
C−(CO)(H)3	−0.3138	N−(Cyclopenty)(H)2	−7.6341
C−(C)(CO)(H)2	−0.3453	N−(Cyclohexy)(H)2	−1.3404
C−(C)2(CO)(H)	−0.0392	N−(C)2(H)	−6.6258
C−(C)3(CO)	0.0843	N−(C)3	−19.2507
C−(C)(O)(H)2	−0.2613	N−(Cb)(H)2	−45.9113
C−(C)2(O)(H)	−0.28	N−(Cb)(C)(H)	−53.226
C−(C)3(O)	−0.3002	N−(Cb)(C)2	−72.0517
CO-(CH3)(O)	8.0703	N−(C)2 correction	2.4901
CO−(CH2)(O)	7.6686	N−(C)3 correction	4.2759
CO−(CH)(O)	5.5291	NI−(Cb)2	6.4393
CO−(O)(H)	8.7052	S−(C)(H)	6.6966
CO−(C)(H)	5.0557	Cl^-	6.4523
CO−(C)2	5.1039	Br^-	11.5556
CO−(Cd)(O)	9.08	ortho correction[b]	0.1705
Cb−(H)	4.7909	meta correction[b]	0.0375
Cb−(C)	−3.3609	cyclopentane correction	0.6152
C−(Cb)(H)3	0.5692	cyclohexane correction	0.4271
C−(Cb)(C)(H)2	0.6996	C_{ob}[c]	0.0652
C−(Cb)(C)2(H)	0.698	C_{mb}[c]	0.1786
C−(Cb)(C)3	1.1613	C_{pb}[c]	0.2004
Cb−(O)	−23.5303	cyclopropane correction	0.8524
O−(Cb)(H)	33.4631	cyclobutane correction	1.054
O−(C)(H)	5.5794	−(CH)< position correction	0.0244
O−(C)2	3.8118	>(C)< position correction	0.0599
O−(CO)(CH3)	−1.8659	double bond position correction	−0.0346
O−(CO)(CH2)	−2.8912	hydroxyl position correction	0.0052
O−(CO)(CH)	−3.0687	benzenamine position correction	−0.5581
O−(CO)(H)	−1.7856	benzene correction	−2.439
phenol position correction	0.0581	*trans* or *cis* structure correction	0.0085
a_2	−0.9719	carbonyl position correction	0.0103
P_0	−124.8429	a_1	128.0716

[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.

$$\mathrm{AD} = \frac{\sum |P_{\mathrm{c,exptl}} - P_{\mathrm{c,pred}}|}{n} \tag{3}$$

$$\delta = \left| \frac{P_{\mathrm{c,exptl}} - P_{\mathrm{c,pred}}}{P_{\mathrm{c,exptl}}} \right| \tag{4}$$

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

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 pressure. The AD for critical pressure P_c predictions of 232 organic compounds is 0.08 MPa, and $\bar{\delta}$ is 2.4 %, which is compared to 0.19 MPa and 5.1 % with the method of Joback, and 0.21 MPa and 5.4 % with the method of Constantinou and Gani.

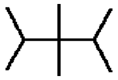
Uncertainty of the New Model. To test the quality of the regressed parameters of the position group contribution equation, the degree of confidence should be calculated. According to the *F* distribution function, the degree of confidence is calculated with the incomplete beta function which could be calculated from the gamma function. The results show that the correlation coefficient is 0.9903; the value of *F* distribution is 231.34; and the degree of confidence is 0.9976, which confirms the greater precision of our position group contribution method which can be used for the best estimation of the critical pressure of organic compounds.

Conclusion

In this work, based on the position group contribution method, a new method recently proposed for the estimation of the critical temperature is extended to the prediction of critical pressure. Contributions for compounds containing carbon, hydrogen, oxygen, nitrogen, sulfur, chlorine, and bromine were reported, and that position compensation factor 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. It is shown that it is possible to use a similar framework to predict the two properties of organic compounds. The predicted results for critical pressure of 232 different organic compounds showed that the position group contribution method performs significantly better than other methods used for comparison.

Appendix A

A.1. Example 1. Estimation of the critical pressure of 2,3,3,4-tetramethylpentane:



This compound is decomposed in position groups as follows: 4 $\mathrm{C{-}(CH)(H)_3}$; 2 $\mathrm{C{-}(C)(H)_3}$; 2 $\mathrm{C{-}(C)_3(H)}$; 1 $\mathrm{C{-}(C)_4}$.

Total number of groups: $N = 9$.

The position factor: position of (CH) group 2, 4, the compensated factor is $P = 2 + 4 = 6$; position of (C) group 3, the position correlation factor is $P = 3$.

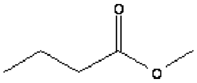
Molecular weight: $M = 128.2551$.

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

$$P_c = -0.1406 \cdot 4 - 0.2478 \cdot 2 - 0.0596 \cdot 2 + 0.2912 \cdot 1 + 0.0244 \cdot 6 + 0.0599 \cdot 3 - {} - 0.9719 \cdot \exp(1/9) + 128.0716 \cdot \exp(1/128.2551) - 124.8429 = 2.59\ \mathrm{MPa}$$

The calculated result is 2.59 Pa, while the experimental critical pressure is 2.72 MPa.

A.2. Example 2. Estimation of the critical pressure of methyl butanoate:



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

Total number of groups: $N = 6$.

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

Molecular weight: $M = 102.1317$.

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

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

		Joback		Constantinou		this work	
chemical family	no. of compounds	AD/MPa	100 $\bar{\delta}$	AD/MPa	100 $\bar{\delta}$	AD/MPa	100 $\bar{\delta}$
alkanes and cycloalkanes	62	0.10	3.5	0.10	3.2	0.08	2.9
alkenes	12	0.08	2.4	0.05	1.8	0.03	0.9
aromatics	13	0.08	2.3	0.07	1.9	0.08	2.2
ketones and aldehydes	20	0.14	3.9	0.18	4.8	0.09	2.7
alcohols	29	0.41	10.9	0.25	6.9	0.07	2.2
acids	9	0.17	5.1	0.20	5.6	0.08	2.8
phenols and ether oxides	11	0.28	7.4	0.33	8.5	0.20	4.7
esters	23	0.18	4.9	0.16	4.4	0.06	1.6
amines and anilines	25	0.34	7.9	0.79	17.0	0.12	2.9
nitriles	5	0.25	8.0	0.24	7.4	0.03	1.0
pyridines	10	0.13	2.9	0.19	4.3	0.06	1.4
bromochloroalkanes and alkane thiols	13	0.41	6.9	0.53	9.9	0.08	1.9
overall	232	0.19	5.1	0.21	5.4	0.08	2.4

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

Table 3. Fully Predictive Estimations of Critical Pressure P_c

compounds	experimental MPa	ref	this work		
			predict	D	100 δ
ethane	4.872	11	4.87	0.00	0.0
propane	4.248	11	4.49	0.24	5.7
n-butane	3.796	11	3.80	0.00	0.0
2-methylpropane	3.64	14	3.77	0.13	3.6
n-pentane	3.37	11	3.33	0.04	1.1
2-methylbutane	3.38	14	3.33	0.05	1.4
2,2-dimethylpropane	3.196	14	3.25	0.05	1.7
n-hexane	3.025	11	2.99	0.03	1.1
2-methylpentane	3.04	14	2.99	0.05	1.6
3-methylpentane	3.12	14	3.04	0.08	2.5
2,2-dimethybutane	3.1	14	3.04	0.06	1.9
2,3-dimethylbutane	3.15	14	3.02	0.13	4.3
n-heptane	2.74	11	2.72	0.02	0.7
2-methylhexane	2.74	14	2.72	0.02	0.7
3-methylhexane	2.81	14	2.77	0.04	1.4
3-ethylpentane	2.89	14	2.80	0.09	3.3
2,2-dimethylpentane	2.77	14	2.77	0.00	0.1
2,3-dimethylpentane	2.91	14	2.77	0.14	4.8
2,4-dimethylpentane	2.74	14	2.77	0.03	1.1
3,3-dimethylpentane	2.95	14	2.96	0.01	0.4
2,2,3-trimethylbutane	2.95	14	2.79	0.16	5.4
n-octane	2.49	11	2.49	0.00	0.2
2-methylheptane	2.5	14	2.49	0.01	0.3
3-methylheptane	2.55	14	2.54	0.01	0.3
4-methylheptane	2.54	14	2.57	0.03	1.1
3-ethylhexane	2.61	14	2.57	0.04	1.6
2,2-dimethylhexane	2.53	14	2.54	0.01	0.5
2,3-dimethylhexane	2.63	14	2.54	0.09	3.3
2,4-dimethylhexane	2.56	14	2.57	0.01	0.3
2,5-dimethylhexane	2.49	14	2.57	0.08	3.1
3,3-dimethylhexane	2.65	14	2.73	0.08	3.2
3,4-dimethylhexane	2.69	14	2.62	0.07	2.7
2-methyl-3-ethylpentane	2.7	14	2.57	0.13	4.9
3-methyl-3-ethylpentane	2.81	14	2.87	0.06	2.0
2,2,3-trimethylpentane	2.73	14	2.59	0.14	5.1
2,2,4-trimethylpentane	2.57	14	2.59	0.02	0.8
2,3,3-trimethylpentane	2.82	14	2.73	0.09	3.1
2,3,4-trimethylpentane	2.73	14	2.59	0.14	5.1
n-nonane	2.29	11	2.30	0.01	0.3
2-methyloctane	2.31	14	2.30	0.01	0.6
4-ethyloctane			2.22		
2,2-dimethyloctane			2.14		
2,3-dimethyloctane			2.17		
2,4-dimethyloctane			2.20		
2,5-dimethyloctane			2.22		
2,6-dimethyloctane			2.24		
2,7-dimethyloctane			2.24		
3,3-dimethyloctane			2.36		
3,4-dimethyloctane			2.25		
3,5-dimethyloctane			2.27		
3,6-dimethyloctane			2.29		
4,4-dimethyloctane			2.42		
3-methyloctane			2.35		
4-methyloctane			2.37		
2-ethylheptane			2.32		
3-ethylheptane			2.37		
4-ethylheptane			2.40		
2,2-dimethylheptane	2.35	14	2.34	0.01	0.2
2,3-dimethylheptane			2.35		
2,4-dimethylheptane			2.37		
2,5-dimethylheptane			2.40		
2,6-dimethylheptane			2.39		
3,3-dimethylheptane			2.54		
3,4-dimethylheptane			2.42		
3,5-dimethylheptane			2.45		
4,4-dimethylheptane			2.60		
3-ethyl-2-metylhexane			2.37		
3-ethyl-3-metylhexane			2.67		
3-ethyl-4-metylhexane			2.45		
4-ethyl-2-metylhexane			2.40		
2,2,3-trimethylhexane			2.39		
2,2,4-trimethylhexane			2.42		
2,2,5-trimethylhexane			2.42		
2,3,3-trimethylhexane			2.54		
2,3,4-trimethylhexane			2.42		
2,3,5-trimethylhexane			2.42		
2,4,4-trimethylhexane			2.60		
3,3,4-trimethylhexane			2.61		
3,3-diethylpentane			2.70		
3-ethyl-2,2-dimethylpentane			2.42		
3-ethyl-2,3-dimethylpentane			2.67		
3-ethyl-2,4-dimethylpentane			2.42		
2,2,3,3-tetramethylpentane	2.74	14	2.58	0.16	5.7
2,2,3,4-tetramethylpentane	2.6	14	2.44	0.16	6.1
2,2,4,4-tetramethylpentane	2.49	14	2.51	0.02	0.9
2,3,3,4-tetramethylpentane	2.72	14	2.59	0.13	5.0
n-decane	2.11	11	2.12	0.01	0.6
2-methylnonane			2.12		
3-methylnonane			2.17		
4-methylnonane			2.20		
5-methylnonane			2.22		
3-ethyloctane			2.20		
3-ethyl-2,2-dimethylhexane			2.57		
3-ethyl-2,3-dimethylhexane			2.52		
3-ethyl-2,4-dimethylhexane			2.27		
3-ethyl-2,5-dimethylhexane			2.27		
3-ethyl-3,4-dimethylhexane			2.57		
4-ethyl-2,2-dimethylhexane			2.27		
4-ethyl-2,3-dimethylhexane			2.17		
4-ethyl-2,4-dimethylhexane			2.55		
4-ethyl-3,3-dimethylhexane			2.46		
2,2,3,3-tetramethylhexane	2.51	14	2.41	0.10	4.0
2,2,3,4-tetramethylhexane			2.29		
2,2,3,5-tetramethylhexane			2.29		

Table 3 Continued

			this work						this work		
compounds	experimental MPa	ref	predict	D	100 δ	compounds	experimental MPa	ref	predict	D	100 δ
4,5-dimethyloctane			2.29			2,2,4,4-tetramethylhexane			2.47		
4-propylheptane			2.22			2,2,5,5-tetramethylhexane	2.19	14	2.40	0.21	9.4
3-ethyl-2-methylheptane			2.20			2,2,4,5-tetramethylhexane			2.32		
3-ethyl-3-methylheptane			2.49			2,3,3,4-tetramethylhexane			2.44		
3-ethyl-4-methylheptane			2.27			2,3,3,5-tetramethylhexane			2.43		
3-ethyl-5-methylheptane			2.30			2,3,4,4-tetramethylhexane			2.47		
4-ethyl-2-methylheptane			2.22			2,3,4,5-tetramethylhexane			2.32		
4-ethyl-3-methylheptane			2.27			3,3,4,4-tetramethylhexane			2.66		
4-ethyl-4-methylheptane			2.66			3,3-dethyl-2-methylpentane			2.57		
5-ethyl-2-methylheptane			2.25			3-ethyl-2,2,3-trimethylpentane			2.65		
2,2,3-trimethylheptane			2.22			3-ethyl-2,2,4-trimethylpentane			2.29		
2,2,4-trimethylheptane			2.24			3-ethyl-2,3,4-trimethylpentane			2.54		
2,2,5-trimethylheptane			2.27			2,2,3,3,4-pentamethylpentane			2.48		
2,2,6-trimethylheptane			2.27			2,2,3,4,4-pentamethylpentane			2.39		
2,3,3-trimethylheptane			2.36			*n*-undecane	1.98	11	1.96	0.02	0.9
2,3,4-trimethylheptane			2.25			*n*-dodecane	1.82	11	1.81	0.01	0.3
2,3,5-trimethylheptane			2.27			*n*-tridecane	1.68	11	1.68	0.00	0.3
2,3,6-trimethylheptane			2.27			*n*-tetradecane	1.57	11	1.54	0.03	1.7
2,4,4-trimethylheptane			2.42			*n*-pentadecane	1.48	11	1.42	0.06	4.2
2,4,5-trimethylheptane			2.29			*n*-hexadecane	1.4	11	1.30	0.10	7.4
2,4,6-trimethylheptane			2.29			*n*-heptadecane	1.34	11	1.18	0.16	12.0
2,5,5-trimethylheptane			2.48			cyclopropane	5.54	14	5.54	0.00	0.0
3,3,4-trimethylheptane			2.44			cyclobutane			4.99		
3,3,5-trimethylheptane	2.32	14	2.46	0.14	6.0	cyclopentane	4.51	14	4.06	0.45	10.1
3,4,4-trimethylheptane			2.47			cyclohexane	4.08	14	3.51	0.57	14.0
3,4,5-trimethylheptane			2.29			methylcyclopentane	3.79	14	3.70	0.09	2.4
3,4-diethylhexane			2.30			methylcyclohexane	3.48	14	3.23	0.25	7.2
3,3-diethylhexane			2.63			ethylcyclopentane	3.4	14	3.44	0.04	1.3
cis-1,2-dimethylcyclopentane			3.45			*trans*-2-heptene			2.85		
trans-1,2-dimethylcyclopentane			3.43			*cis*-3-heptene			2.87		
cis-1,3-dimethylcyclopentane			3.48			*trans*-3-heptene			2.85		
trans-1,3-dimethylcyclopentane			3.46			1-octene	2.68	15	2.64	0.04	1.3
1,1-dimethylcyclopentane			3.54			*cis*-2-octene			2.60		
1,1-dimethylcyclohexane			3.12			*trans*-2-octene			2.58		
cis-1,2-dimethylcyclohexane			3.03			*cis*-3-octene			2.60		
trans-1,2-dimethylcyclohexane			3.01			*trans*-3-octene			2.58		
cis-1,3-dimethylcyclohexane			3.05			*cis*-4-octene			2.57		
trans-1,3-dimethylcyclohexane			3.04			*trans*-4-octene			2.55		
cis-1,4-dimethylcyclohexane			3.08			1-nonene			2.43		
trans-1,4-dimethylcyclohexane			3.06			1-decene	2.22	15	2.25	0.03	1.3
ethylcyclohexane			3.02			1-undecene			2.08		
n-propylcyclopentane			3.02			1-dodecene	1.93	15	1.92	0.01	0.3
n-propylcyclohexane			2.82			1,3-butadiene	4.32	15	4.32	0.00	0.0
n-butylcyclopentane			3.01			benzene	4.895	12	4.94	0.05	0.9
n-butylcyclohexane			2.64			methylbenzene	4.108	12	4.10	0.01	0.3
n-pentylcyclopentane			2.83			1,4-dimethylbenzene	3.511	12	3.43	0.08	2.3
n-pentylcyclohexane			2.48			1,2-dimethylbenzene	3.732	12	3.60	0.13	3.5
n-hexylcyclopentane			2.67			1,3-dimethylbenzene	3.541	12	3.47	0.07	2.1
n-heptylcyclohexane			2.52			ethylbenzene	3.609	12	3.72	0.11	3.2
1-butene	4.02	15	4.09	0.07	1.8	1,2,3-trimethylbenzene	3.454	12	3.32	0.13	3.9
cis-2-butene	4.21	15	4.15	0.06	1.3	1,2,4-trimethylbenzene	3.232	12	3.15	0.08	2.6
trans-2-butene	4.1	15	4.14	0.04	0.9	1,3,5-trimethylbenzene	3.127	12	3.05	0.07	2.4

Table 3 Continued

			this work						this work		
compounds	experimental MPa	ref	predict	*D*	100 δ	compounds	experimental MPa	ref	predict	*D*	100 δ
1-pentene	3.56	15	3.57	0.01	0.2	1,2,3,4-tetramethylbenzene			3.21		
cis-2-pentene			3.61			1,2,3,5-tetramethylbenzene			3.07		
trans-2-pentene			3.60			1,2,4,5-tetramethylbenzene			3.03		
2-methyl-1-butene			3.45			1-methyl-2-ethylbenzene			3.36		
2-methyl-2-butene	3.42	15	3.47	0.05	1.4	1-methyl-3-ethylbenzene			3.23		
3-methyl-1-butene	3.53	15	3.53	0.00	0.0	1-methyl-4-ethylbenzene	3.23	12	3.19	0.04	1.2
1-hexene	3.21	15	3.19	0.02	0.7	*n*-propylbenzene	3.2	12	3.32	0.12	3.6
cis-2-hexene			3.19			isopropylbenzene	3.209	12	3.24	0.03	0.9
trans-2-hexene			3.18			1-methyl-2-isopropylbenzene			2.99		
cis-3-hexene			3.20			1-methyl-3-isopropylbenzene			2.85		
trans-3-hexene			3.18			1-methyl-4-isopropylbenzene			2.82		
2-methyl-1-hexene			2.80			*n*-butylbenzene	2.89	12	2.96	0.07	2.4
3-methyl-1-hexene			2.95			*sec*-butylbenzene			2.91		
4-methyl-1-hexene			2.96			*tert*-butylbenzene			2.97		
1-heptene	2.92	15	2.89	0.03	1.0	*n*-pentylbenzene			2.65		
cis-2-heptene			2.87			*n*-hexylbenzene			2.37		
n-heptylbenzene			2.11			2-tridecanone			1.67		
butanone	4.207	16	4.27	0.06	1.5	3-tridecanone			1.62		
2-pentanone	3.683	16	3.70	0.02	0.5	4-tridecanone			1.63		
3-pentanone	3.729	16	3.65	0.07	2.0	5-tridecanone			1.64		
3-methyl-2-butanone	3.8	16	4.00	0.20	5.4	6-tridecanone			1.65		
2-hexanone	3.3	16	3.27	0.03	0.8	7-tridecanone			1.66		
3-hexanone	3.32	16	3.22	0.10	2.9	2-tetradecanone			1.52		
3,3-dimethyl-2-butanone	3.43	16	3.43	0.00	0.0	3-tetradecanone			1.47		
4-methyl-2-pentanone	3.27	16	3.01	0.26	8.0	4-tetradecanone			1.48		
2-heptanone	2.97	16	2.94	0.03	1.0	7-tetradecanone			1.51		
3-heptanone			2.89			propanal	5.26	16	5.27	0.01	0.2
4-heptanone			2.90			butanal	4.32	16	4.47	0.15	3.5
2-octanone			2.66			1-pentanal	3.97	16	3.91	0.06	1.6
3-octanone			2.61			1-hexanal	3.46	16	3.49	0.03	0.8
4-octanone			2.62			1-heptanal	3.16	16	3.15	0.01	0.4
2-methyl-3-hexanone			3.17			1-octanal	2.96	16	2.87	0.09	3.1
5-methyl-2-hexanone			3.01			1-nonanal	2.68	16	2.63	0.05	2.0
2,4-dimethyl-3-pentanone			3.50			1-decanal	2.6	16	2.41	0.19	7.2
2-methyl-3-heptanone			3.15			2-methylpropanal	5.1	16	4.75	0.35	7.0
5-methyl-3-heptanone			2.87			2-methylhexanal			3.15		
2,5-dimethyl-3-hexanone			2.96			3-methylhexanal			3.20		
5-nonanone	2.32	16	2.39	0.07	3.0	ethanol	6.137	13	6.11	0.03	0.5
4-nonanone			2.38			1-propanol	5.169	13	5.04	0.13	2.6
3-nonanone			2.37			2-propanol	4.764	13	4.95	0.18	3.8
2-nonanone	2.48	16	2.42	0.06	2.6	1-butanol	4.414	13	4.33	0.08	1.8
2,6-dimethyl-4-heptanone			2.48			2-butanol	4.202	13	4.27	0.07	1.6
2-decanone			2.20			2-methyl-1-propanol	4.295	13	4.33	0.04	0.9
3-decanone			2.15			2-methyl-2-propanol	3.972	13	4.22	0.25	6.2
4-decanone			2.17			1-pentanol	3.897	13	3.83	0.07	1.8
5-decanone			2.18			2-pentanol	3.675	13	3.76	0.09	2.4
2-undecanone			2.01			3-pentanol			3.79		
3-undecanone			1.96			2-methyl-1-butanol	3.94	13	3.85	0.09	2.2
4-undecanone			1.97			3-methyl-1-butanol	3.93	13	3.85	0.08	2.0
5-undecanone			1.98			2-methyl-2-butanol	3.71	13	3.74	0.03	0.8
6-undecanone			1.99			3-methyl-2-butanol	3.87	13	3.79	0.08	2.2
2-dodecanone			1.83			1,2-butanedial			4.57		

Table 3 Continued

			this work						this work		
compounds	experimental MPa	ref	predict	D	100 δ	compounds	experimental MPa	ref	predict	D	100 δ
3-dodecanone			1.79			1,3-butanedial			4.55		
4-dodecanone			1.80			1-hexanol	3.417	13	3.43	0.02	0.5
5-dodecanone			1.81			2-hexanol	3.31	13	3.37	0.06	1.8
6-dodecanone			1.82			3-hexanol	3.36	13	3.40	0.04	1.2
2-methyl-1-pentanol	3.45	13	3.46	0.01	0.3	isopropyl methyl ether	3.762	16	3.74	0.03	0.7
4-methyl-1-pentanol			3.48			ethyl *n*-propyl ether	3.37	16	3.33	0.04	1.8
2-methyl-2-pentanol			3.35			butyl methyl ether	3.37	16	3.38	0.01	0.3
2-methyl-3-pentanol	3.46	13	3.37	0.09	2.6	methyl pentyl ether	3.042	16	3.03	0.01	0.4
4-methyl-2-pentanol			3.42			butyl ethyl ether			2.98		
3-methyl-3-pentanol	3.52	13	3.37	0.15	4.3	dipropyl ether	3.028	16	2.98	0.05	1.6
1-heptanol	3.058	13	3.12	0.06	1.9	diisopropyl ether	2.832	16	2.79	0.05	1.6
2-heptanol	3.021	13	3.05	0.03	1.0	methyl formiate	6	16	6.00	0.00	0.1
3-heptanol			3.08			methyl acetate	4.75	16	4.71	0.04	0.8
4-heptanol			3.09			ethyl formiate	4.74	16	4.78	0.04	0.8
1-octanol	2.777	13	2.85	0.07	2.5	propyl formiate	4.06	16	4.20	0.14	3.4
2-octanol	2.754	13	2.78	0.03	1.0	*n*-pentyl methanoate	3.46	16	3.41	0.05	1.5
3-octanol			2.81			ethyl acetate	3.87	16	3.86	0.01	0.4
4-octanol			2.82			methyl propionate	4	16	3.98	0.02	0.5
2-ethyl-1-hexanol	2.8	13	2.90	0.10	3.5	propyl acetate	3.36	16	3.44	0.08	2.3
1-nonanol	2.528	13	2.61	0.09	3.4	isopropyl acetate	3.31	16	3.31	0.00	0.1
2-nonanol	2.53	13	2.55	0.02	0.7	methyl butanoate	3.47	16	3.55	0.08	2.4
3-nonanol			2.58			methyl isobutanoate	3.43	16	3.42	0.01	0.3
4-nonanol			2.56			2-propenyl acetate			3.94		
1-decanol	2.315	13	2.41	0.09	3.9	2-ethenyl acetate	4.185	16	4.19	0.00	0.0
2-decanol			2.34			ethyl propionate	3.45	16	3.32	0.13	3.7
3-decanol			2.37			butyl acetate	3.14	16	3.10	0.04	1.2
4-decanol			2.38			pentyl ethanoate	2.73	16	2.82	0.09	3.5
5-decanol			2.38			propyl propionate	3.06	16	3.00	0.06	2.0
1-undecanol	2.147	13	2.22	0.07	3.3	ethyl butanoate	3.1	16	3.01	0.09	2.9
1-dodecanol	1.994	13	2.04	0.05	2.5	propyl butanoate	2.72	16	2.74	0.02	0.6
phenol	5.93	16	5.38	0.55	9.2	ethyl isobutanoate	3.1	16	3.23	0.13	4.1
o-cresol	4.17	16	4.59	0.42	10.2	methyl pentanoate	3.2	16	3.22	0.02	0.5
m-cresol	4.36	16	4.65	0.29	6.7	ethyl pentanoate			2.75		
p-cresol	4.07	16	4.71	0.64	15.7	propyl pentanoate			2.51		
2,3-xylenol			4.26			isobutyl acetate	2.99	16	3.05	0.06	2.2
2,4-xylenol			4.19			1 methylpropyl ethanoate	3.01	16	3.01	0.00	0.1
2,5-xylenol			4.21			isobutyl acrylate			2.95		
2,6-xylenol			4.30			isobutyl butyrate			2.45		
3,4-xylenol			4.38			isobutyl formate	3.88	16	3.71	0.17	4.4
3,5-xylenol			4.30			diphenyl ether			3.08		
3-ethylphenol			4.24			methylamine			7.42		
2-ethylphenol			4.18			dimethylamine	5.34	18	5.34	0.00	0.0
4-ethylphenol			4.30			ethanamine	5.6	18	6.36		
diethyl ether	3.644	16	3.78	0.14	3.8	propylamine	4.74	18	5.15	0.41	8.7
isopropylamine	4.55	18	4.95	0.40	8.9	2,6-dimethylpyridine	3.85	18	3.85	0.00	0.1
trimethylamine	4.08	18	4.08	0.00	0.0	3,4-dimethylpyridine	4.2	18	4.10	0.10	2.4
butylamine	4.2	18	4.37	0.17	4.1	3,5-dimethylpyridine	4.05	18	4.08	0.03	0.7
isobutylamine			4.40			propanenitrile	4.26	18	4.19	0.07	1.6
sec-butylamine	5	18	4.50	0.50	10.0	butanenitrile	3.88	18	3.87	0.01	0.3
tert-butylamine	3.85	18	3.85	0.00	0.0	2-methylpropanenitrile			3.46		
diethylamine	3.754	18	3.72	0.03	0.8	pentanenitrile	3.58	18	3.57	0.01	0.2
pentylamine			3.81			3-methylbutanenitrile			3.62		

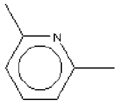
Table 3 Continued

			this work						this work		
compounds	experimental MPa	ref	predict	D	100 δ	compounds	experimental MPa	ref	predict	D	100 δ
cyclopentylamine			3.61			2,2-dimethylpropanenitrile			2.79		
hexylamine			3.38			hexanenitrile	3.3	18	3.32	0.02	0.7
1-octanamine	2.6	18	2.75	0.15	5.7	octanenitrile	2.85	18	2.91	0.06	2.2
butyl ethylamine			0.95			decanenitrile			2.58		
isopropyl propylamine			2.39			chloroethane	5.2	19	5.27	0.07	1.4
triethylamine	3.03	18	3.03	0.00	0.0	1-chloropropane	4.57	19	4.44	0.13	2.9
dipropylamine	3.63	18	3.49	0.14	3.8	2-chloropropane	4.26	19	4.25	0.01	0.3
diisopropylamine			3.25			1-chlorobutane			3.85		
cyclohexylamine			4.20			2-chlorobutane			3.69		
dibutylamine	3.11	18	3.28	0.17	5.4	2-chloro-2-methylpropane			3.96		
1,2-ethanediamine	6.71	18	6.32	0.39	5.8	1-chloropentane			3.41		
1,3-propanediamine	5.6	18	5.31	0.29	5.2	2-chloropentane			3.25		
1,4-butanediamine	4.5	18	4.57	0.07	1.7	1-chlorohexane			3.06		
1,6-hexanediamine	3.6	18	3.56	0.04	1.2	1-cloroheptane			2.77		
1,8-octanediamine	2.8	18	2.86	0.06	2.2	1-chloro-3-methylbutane			4.19		
1,9-nonanediamine	2.6	18	2.58	0.02	0.8	1,1-dichloroethane			5.10		
1,10-decanediamine	2.4	18	2.33	0.07	2.9	bromoethane	5.8	19	5.80	0.00	0.0
1,12-dodecanediamine	2	18	1.90	0.10	5.0	1-bromopropane	4.8	19	4.80	0.00	0.0
benzenamine	5.63	18	5.63	0.00	0.0	2-bromopropane			5.68		
2-methylbenzenamine	4.7	18	4.70	0.00	0.0	1-bromobutane			4.12		
3-methylbenzenamine	4.2	18	4.20	0.00	0.0	1-bromo-2-methylpropane			4.12		
N-methylbenzenamine	5.2	18	5.20	0.00	0.0	2-bromo-2-methylpropane			4.64		
N-ethylbenzenamine			4.79			1-bromopentane			3.61		
N,*N*-dimethylbenzenamine	3.6	18	3.60	0.00	0.0	methylthio ethane			3.07		
N,*N*-diethylbenzenamine			2.93			1-methylthio propane			2.78		
pyridine	5.65	18	5.60	0.05	0.8	2-methylthio propane			2.85		
2-methylpyridine	4.62	18	4.60	0.02	0.5	1-methylthio butane			2.54		
3-methylpyridine	4.65	18	4.71	0.06	1.3	2-methyl-2-methylthio propane			2.58		
4-methylpyridine	4.67	18	4.73	0.06	1.3	1-ethylthio propane			2.02		
2,3-dimethylpyridine	4.1	18	3.97	0.13	3.3	2-ethylthio propane			2.10		
2,4-dimethylpyridine	3.95	18	3.99	0.04	1.0	1-ethylthio butane			1.76		
2,5-dimethylpyridine	3.85	18	3.97	0.12	3.0	2-ethylthio butane			1.76		
2-ethylthio-2-methyl propane			1.86			cyclopentanethiol			4.37		
methylthio cyclopentane			3.14			1-hexanethiol			3.19		
1,2-dibromopropane			1.51			2-methyl-2-pentanethiol			3.37		
1,1,2-trichloroethane			1.01			2,3-dimethyl-2-butanethiol			3.39		
methylthio methane	7.23	17	4.56			cyclohexanethiol			3.82		
ethanethiol	5.49	17	5.50	0.01	0.2	1-heptanethiol			2.89		
1-propanethiol	4.6	17	4.62	0.02	0.5	1-octanethiol			2.63		
2-propanethiol			4.70			acetic acid	5.78	16	5.73	0.05	0.9
1-butanethiol	4	17	4.01	0.01	0.3	*n*-propanoic acid	4.67	16	4.70	0.03	0.7
2-butanethiol			4.11			acrylic acid			5.66		
2-methyl-1-propanethiol			4.01			*n*-butyric acid	4.06	16	4.12	0.06	1.4
2-methyl-2-propanethiol			4.06			*n*-pentanoic acid	3.63	16	3.68	0.05	1.3
1-pentanethiol			3.55			2-ethyl butyric acid			3.35		
2-methyl-1-butanethiol			3.58			2-ethyl hexanoic acid	2.78	16	2.87	0.09	3.4
3-methyl-1-butanethiol		17	3.36			*n*-hexanoic acid	3.38	16	3.32	0.06	1.6
2-methyl-2-butanethiol			3.73			*n*-heptanoic acid	3.16	16	3.03	0.13	4.0
3-methyl-2-butanethiol			3.68			*n*-octanoic acid	2.87	16	2.78	0.09	3.0
2,2-dimethyl-1-propanethiol			3.60			*n*-nonanoic acid	2.35	16	2.56	0.21	9.1

$$\begin{gathered}P_c = -0.1151\cdot 1 - 0.0882\cdot 1 - 0.3453\cdot 1 - 0.2372\cdot 1 + \\ 7.6686\cdot\tanh(1/6) + 0.0103\cdot 4 - \\ - 1.8659\cdot\tanh(1/6) - 0.9719\cdot\exp(1/6) + \\ 128.0716\cdot\exp(1/102.1317) - 124.8429 = 3.55\ \text{MPa}\end{gathered}$$

Therefore, the calculated result is 3.55 MPa while the experimental critical pressure is 3.47 MPa.

A.3. Example 3. Estimation of the critical pressure of 2,6-dimethylpyridine



This compound could be decomposed in position groups as follows: 3 Cb−H; 2 Cb−(C); 2 $C-(Cb)(H)_3$; 1 $NI-(Cb)_2$; 2 Cob correction; 1 benzene correction.

Total number of groups: $N = 8$.

Molecular weight: $M = 107.1531$.

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

$$\begin{gathered}P_c = 4.7909\cdot\tanh(3/8) - 3.3609\cdot\tanh(2/8) + 0.5692\cdot 2 + \\ 6.4393\cdot\tanh(1/8) + \\ + 0.0652\cdot 2 - 2.439 - 0.9719\cdot\exp(1/8) + \\ 128.0716\cdot\exp(1/107.1531) - 124.8429 = 3.85\ \text{MPa}\end{gathered}$$

So, the calculated result is 3.85 MPa, while the experimental critical pressure is 3.85 MP.

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