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Method for Estimating Critical Pressure[†]

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A new method is suggested to estimate the critical pressure of non-associative fluids. It is based on the extrapolation of the function fitted over the range of standard conditions up to the critical temperature. The approximate equation for the logarithm of pressure is based on the expansion of the Haggenmacher's formula for the difference between specific volumes of saturated liquid and vapor into series that consists of first and forth powers of the inverse reduced temperature. It has been shown that such a combination provides a clear minimum for the error of approximation. Calculation of the critical pressure for 109 substances of various classes (*n*-alkanes, halogensubstituted hydrocarbons, alkylbenzenes, etc.) has been evaluated with the proposed approximation. The results are in quite good agreement with the experimental data.

Introduction

The critical pressure P_c is an important constant that plays a prominent role in the prediction of physicochemical properties of the substances. However, the experimental determination of this parameter has significant difficulties. Moreover, it is impossible for certain classes of liquids since they are thermally unstable in the critical region.

Owing to an absence of reliable experimental results, one needs the various methods of approximation of the critical pressure using the data in the range of standard conditions. Recently, the additive methods of approximation are most popular.[1−8] At the same time, the additive approach is not unique. The prognosis methods based on the usage of other thermodynamic properties such as density, vapor pressure, and enthalpy of vaporization at the boiling point are very important as well.

In our opinion, it is possible to use the method that represents the dependence of reduced pressure $P_r = P/P_c$ on the reduced temperature $T_r = T/T_c$ in the form

$$\ln\left(\frac{P}{P_c}\right) = f(T_r^{-1}) \tag{1}$$

to estimate of the critical pressure for organic liquids. It is obvious that the critical point has coordinates (0, 1) in the coordinate plane ($\ln(P_r)$, T_r). This means that the right side of the eq 1 can be calculated using the curve fitted over the range from T_1 to T_2 if this curve is passed through (0, 1) after the substitution of P_s and T_s into eq 1.

Clearly, the explicit expression of the right side of eq 1 depends on the temperature range [T_1, T_2]: an approximation is more exact if this interval is large and T_2 is close to T_c. But as a rule, experimental research deals with a narrow temperature range. Usually the results are represented in reference papers as the coefficients of Antoine equation. The area of applicability of these coefficients corresponds to the pressure range from (10 to 1500) mmHg, where the Antoine equation has the best correlation with experimental data for the vapor pressure. For this reason, we use the interval from (10 to 1500) mmHg as a basic one in our method of estimation of the critical pressure.

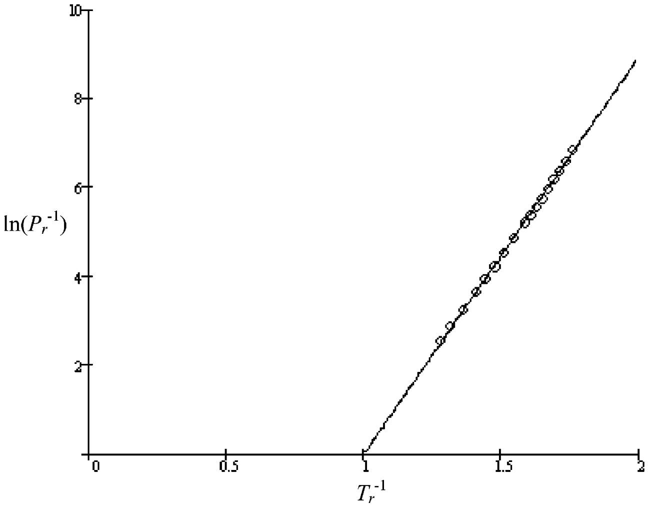

Figure 1. Dependence of the logarithm of inverse reduced pressure on the inverse reduced temperature for *n*-undecane.

Expansion of Reduced Pressure in Terms of Inverse Reduced Temperature

Let us consider the Clapeyron−Clausius equation:

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

It can be represented in the reduced form as

$$\frac{dP_r}{dT_r} = \frac{P_r}{T_r^2}\frac{\Delta H}{RT_c\Delta Z} \tag{2}$$

where $P_r = P/P_c$, $T_r = T/T_c$, and the critical values are marked with the subscript "c".

It is well-known that the complex $\Delta H/\Delta Z$ is almost constant for a large range of temperature except in the

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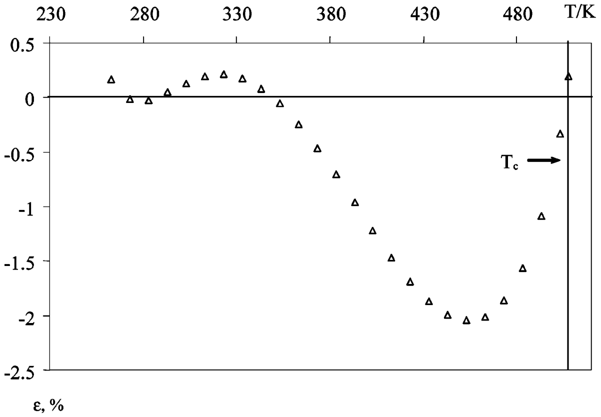

Figure 2. Dependence of $\epsilon = (P_{calc} - P_{exp})/(P_{exp})\cdot 100$ % on the temperature for *n*-hexane.

Table 1. Values of Critical Pressures for *n*-Alkanes Obtained Using Equation 7

compound	T_c/K exp[11]	P_c/MPa exp[11]	P_c/MPa calcd (eq 7)
methane	190.954 ± 0.015	4.599 ± 0.003	4.35
ethane	305.32 ± 0.04	4.872 ± 0.01	4.72
propane	369.83 ± 0.1	4.248 ± 0.01	4.22
n-butane	425.12 ± 0.1	3.796 ± 0.01	3.72
n-pentane	469.7 ± 0.2	3.370 ± 0.02	3.36
n-hexane	507.6 ± 0.2	3.025 ± 0.02	3.02
n-heptane	540.2 ± 0.3	2.74 ± 0.03	2.75
n-octane	568.7 ± 0.3	2.49 ± 0.03	2.49
n-nonane	594.6 ± 0.6	2.29 ± 0.05	2.29
n-decane	617.7 ± 0.6	2.11 ± 0.05	2.08
n-undecane	639 ± 1	1.98 ± 0.1	1.95
n-dodecane	658 ± 1	1.82 ± 0.1	1.81
n-tridecane	675 ± 1	1.68 ± 0.1	1.66
n-tetradecane	693 ± 2	1.57 ± 0.2	1.57
n-pentaradecane	708 ± 2	1.48 ± 0.2	1.47
n-hexadecane	723 ± 2	1.40 ± 0.2	1.39
n-heptadecane	736 ± 2	1.34 ± 0.2	1.33
n-octadecane	747 ± 3	1.29 ± 0.2	1.26
n-nonadecane	755 ± 8	1.16 ± 0.2	1.18
n-eicosane	768 ± 8	1.07 ± 0.2	1.11

Table 2. Values of Critical Pressures for Cyclic and Branch Alkanes Obtained Using Equation 7

compound	T_c/K exp[9,13]	P_c/MPa exp[9,13]	P_c/MPa calcd (eq 7)
cyclopropane	398.0 ± 0.3	5.54 ± 0.05	5.54
cyclopentane	511.7 ± 0.2	4.51 ± 0.04	4.52
cyclohexane	554 ± 1	4.07 ± 0.05	4.13
cycloheptane	604.2 ± 0.5	3.82 ± 0.04	3.80
methylcyclopentane	532.7 ± 0.2	3.79 ± 0.04	3.78
ethylcyclopentane	569.5 ± 0.5	3.40 ± 0.04	3.41
methylcyclohexane	573 ± 1	3.48 ± 0.02	3.48
2,2-dimethylbutane	489 ± 0.5	3.10 ± 0.02	3.03
2,3-dimethylbutane	500.1 ± 0.5	3.15 ± 0.08	3.11
2-methylpentane	497.8 ± 0.4	3.03 ± 0.07	2.99
3-methylpentane	504 ± 4	3.11 ± 0.06	3.06
2-methylhexane	530.5 ± 0.5	2.74 ± 0.02	2.66
3-methylhexane	535.2 ± 0.4	2.81 ± 0.04	2.77
4-methylheptane	561.7 ± 0.5	2.54 ± 0.04	2.53
2-methylheptane	559.7 ± 0.1	2.50 ± 0.02	2.48
2,2,4-trimethylpentane	543.9 ± 0.4	2.57 ± 0.04	2.54
2,2-dimethylpentane	520.5 ± 0.5	2.77 ± 0.05	2.75
2,3-dimethylpentane	537.3 ± 0.5	2.91 ± 0.05	2.89
2,4-dimethylpentane	519.8 ± 0.5	2.74 ± 0.05	2.71
3,3-dimethylpentane	536.4 ± 0.5	2.95 ± 0.05	2.92
2-methylbutane	461 ± 5	3.38 ± 0.05	3.32
3-methylheptane	563.6 ± 0.5	2.55 ± 0.04	2.53
2,2,3-trimethylbutane	531.1 ± 0.3	2.95 ± 0.05	2.91
2,3,4-trimethylpentane	566.4 ± 0.5	2.73 ± 0.04	2.70
2,3-dimethylhexane	563.5 ± 0.5	2.63 ± 0.04	2.60
2,5-dimethylhexane	550.0 ± 0.5	2.49 ± 0.02	2.54
2,4-dimethylhexane	553.5 ± 0.5	2.56 ± 0.04	2.53
3,4-dimethylhexane	568.8 ± 0.5	2.69 ± 0.04	2.66
2,2-dimethylpropane	433.8 ± 0.1	3.20 ± 0.01	3.10

Table 3. Values of Critical Pressures for Aromatics Obtained Using Equation 7

compound	T_c/K exp[9,14]	P_c/MPa exp[9,14]	P_c/MPa calcd (eq 7)
benzene	562.05 ± 0.07	4.895 ± 0.06	4.89
toluene	591.75 ± 0.15	4.108 ± 0.01	4.22
o-xylene	630.3 ± 0.5	3.732 ± 0.04	3.74
m-xylene	617 ± 0.5	3.541 ± 0.04	3.52
p-xylene	616.2 ± 0.2	3.511 ± 0.02	3.47
ethylbenzene	617.15 ± 0.1	3.609 ± 0.01	3.59
isopropylbenzene	631 ± 0.5	3.209 ± 0.04	3.24
butylbenzene	660.5 ± 0.5	2.89 ± 0.04	2.85
1,2,3-trimethylbenzene	664.5 ± 0.5	3.454 ± 0.04	3.39
1,3,5-trimethylbenzene	637.3 ± 0.5	3.127 ± 0.04	3.10
1,2,4-trimethylbenzene	649.1 ± 0.5	3.232 ± 0.04	3.21
naphthalene	748.4 ± 0.5	4.05 ± 0.05	4.06
p-resol	704.55	4.559	4.44
o-resol	697.55	4.17	4.33

Table 4. Values of Critical Pressures for Alkenes Obtained Using Equation 7

compound	T_c/K exp[9,15]	P_c/MPa exp[9,15]	P_c/MPa calcd (eq 7)
ethylene	282.5 ± 0.5	5.06 ± 0.05	4.94
propene	365.2 ± 0.8	4.60 ± 0.03	4.62
1-butene	419.5 ± 0.5	4.02 ± 0.05	4.02
1-pentene	464.8 ± 0.5	3.56 ± 0.05	3.49
1-hexene	504.0 ± 0.3	3.21 ± 0.03	3.14
1-heptene	537.3 ± 0.4	2.92 ± 0.04	2.83
1-octene	567.0 ± 0.8	2.68 ± 0.08	2.58
1-nonene	594.0 ± 1.0	2.28	2.38
1-decene	617.0 ± 2.0	2.22 ± 0.1	2.15
1-dodecene	658.0 ± 2.0	1.93 ± 0.2	1.84

neighborhood of the critical point. That leads to the widely used equation:

$$\ln P_r = A - \frac{B}{T_r} \tag{3}$$

To check eq 2 as a predictor, we use the data on vapor pressure and the critical properties of *n*-alkanes presented in the NIST Chemistry WebBook database[9] and in refs 10 and 11. The search of the desired parameter is based on the numerical variation of the value of critical pressure using MathCAD 2000 Professional.

As an example, Figure 1 represents the graph of eq 2 for *n*-undecane, based on the vapor pressure data from ref 10. The *n*-undecane's critical temperature[11] is 639 K. As a result, we have $P_c = 25.85$ bar. The corresponding experimental value is $P_c = 19.8$ bar. One can see that the last one is 25.5 % less than the result of the calculation. Analogously, there is a large error for many liquids if one uses first approximation (eq 3).

Let us consider the next approximation. Haggenmacher[12] showed that the dependence

$$\Delta Z = \left(1 - \frac{P_r}{T_r^3}\right)^{1/2} \tag{4}$$

is a good approximation for the reduced relative volume in a large interval of temperatures and pressures. Using the Taylor expansion of eq 4, it is possible to get the expansion of eq 2 in terms of inverse reduced temperatures in the following form:

$$\frac{dP_r}{dT_r} = \frac{P_r}{T_r^2}\frac{\Delta H}{RT_c}\left(1 + \frac{P_r}{2T_r^3} - \frac{1}{4}\left(\frac{P_r}{T_r^3}\right)^2 + ...\right) \tag{5}$$

Table 5. Values of Critical Pressures for Alcohols Obtained Using Equation 7

compound	T_c/K exp[16,17]	P_c/MPa exp[16,17]	P_c/MPa calcd (eq 7)
methanol	512.5 ± 0.2	8.084 ± 0.02	8.61
ethanol	514.0 ± 0.2	6.137 ± 0.02	7.37
propanol	536.8 ± 0.3	5.169 ± 0.02	6.34
n-butanol	563.0 ± 0.3	4.414 ± 0.02	5.49
n-pentanol	588.1 ± 0.5	3.897 ± 0.02	4.60
n-hexanol	610.3 ± 0.5	3.417 ± 0.02	3.79
n-heptanol	632.6 ± 0.5	3.058 ± 0.02	3.19
n-octanol	652.5 ± 0.5	2.777 ± 0.03	2.78
n-nonanol	670.7 ± 1	2.528 ± 0.05	2.46
n-decanol	687.3 ± 1	2.315 ± 0.05	2.16
n-undecanol	703.6 ± 1.5	2.147 ± 0.05	2.00
n-dodecanol	719.4 ± 1.5	1.994 ± 0.05	1.86
n-tridecanol	732 ± 7	1.79 ± 0.05	1.70
n-tetradecanol	743 ± 7	1.67 ± 0.05	1.56
n-pentaradecanol	757 ± 8	1.60 ± 0.05	1.50
n-hexadecanol	770 ± 8	1.46 ± 0.04	1.47
n-heptadecanol	780 ± 8	1.35 ± 0.04	1.37
n-octadecanol	790 ± 8	1.28 ± 0.04	1.33
n-nonadecanol	808 ± 8	1.15 ± 0.03	1.19

Table 6. Values of Critical Pressures for Nitrogen Compounds Obtained Using Equation 7

compound	T_c/K exp[18]	P_c/MPa exp[18]	P_c/MPa calcd (eq 7)
pyridine	620.0 ± 0.4	5.65 ± 0.02	5.65
4-methylpyridine	646.0 ± 0.5	4.65 ± 0.1	4.62
2,3-dimethylpyridine	655.5 ± 0.3	4.10 ± 0.05	4.44
2,5-dimethylpyridine	644.3 ± 0.3	3.85 ± 0.05	3.85
3,4-dimethylpyridine	683.7 ± 0.3	4.20 ± 0.05	4.40
3,5-dimethylpyridine	667.7 ± 0.3	4.05 ± 0.05	4.16
benzenamine	705 ± 2	5.63 ± 0.05	5.66
2-methylbenzenamine	717 ± 3	4.7 ± 0.1	5.08

Table 7. Values of Critical Pressures for Halohydrocarbons Obtained Using Equation 7

compound	T_c/K exp[9]	P_c/MPa exp[9]	P_c/MPa calcd (eq 7)
chlorobenzene	632.35	4.5191	4.50
bromobenzene	670	4.401	4.28
fluoromethane	317.28	5.897	5.84
dichloromethane	508	6.355	6.36
perfluoroethane	293.03	3.013	3.01
perfluorobenzene	517	3.3	3.27
tetrachloromethane	556.5	4.5576	4.61
trifluoromethane	299.293	4.832	4.85
difluoromethane	351.255	5.782	5.78
1,1-difluoroethane	386.411	4.51675	4.50
1,1,1,2-tetrafluoroethane	374.21	4.05928	4.10
1-chloro-1,1-difluoroethane	410.26	4.0700	4.07

Table 8. Correlating Accuracy by Equation 7 for 112 Compounds Divided into Eight Classes

compound type	no.	± Δ MPa	<ε> %	deviations distributions ε <1	1−2	2−3	3−4	4−5	>5
n-alkanes	20	0.07	1.3	11	5	1	2	0	1
cyclic alkanes and branch alkanes	29	0.04	1.1	11	14	3	1	0	0
aromatics	14	0.07	1.3	8	3	2	1	0	0
alkenes	10	0.09	2.6	2	1	2	3	2	0
alcohols	19	0.53	8.2	2	1	1	2	1	12
nitrogen compounds	8	0.21	3.1	4	0	1	0	1	2
halohydrocarbons	12	0.04	0.7	9	2	1	0	0	0

Taking into account the weak and compensatory dependence of ΔH and P_r on the temperature if the region of parameters is far from the critical point, we can keep only the first variable term in the parentheses in eq 5. Thus, the next approximation after eq 4 is

$$\ln P_r = A - \frac{B}{T_r} + \frac{C}{T_r^{\,4}} \qquad (6)$$

where A, B, and C are constants.

In a general case, we can represent eq 5 as an expansion with the temperature-dependent coefficients. In using eq 3 as a limiting case, we collect this dependence in $C = C(\Delta H, P_c, T_r^{-1})$. But an empirical study of a large set of experimental data shows that this combination is a constant with a good exactness up to the critical point. This allowed us to use eq 6 for approximation if the reduced temperature and pressure are varied in a large range and to calculate the critical pressure.

The algorithm is the following. Since $P_r(1) = 1$, then $A = B - C$, and eq 6 takes the following form:

$$\ln P = \ln P_c + B(1 - T_r^{-1}) - C(1 - T_r^{-4}) \qquad (7)$$

Knowing the value of T_c, we fit the function ln $P(T_r^{-1})$ using the approximation (eq 7) from the set of experimental data in the non-critical range. That gives us the values of the unknown parameters B, C, and ln P_c. The logarithm of the last one is the desirable value. For the example on *n*-undecane considered above. the calculation using eq 7 leads to the value $P_c = 19.54$ bar, which has a difference of 1.3 % from the experimental one.

It can be pointed out that eq 3 does not allow us to describe the dependence $P = f(T)$ everywhere over the range from 10 mmHg to P_c (see the typical error‘s curve in Figure 2, but this error tends to be minimal around the critical point. Therefore, expansion (eq 7) could be used for the estimation of the critical pressure.

Comparison with the Experiment

Obliviously, the prognostic exactness of calculations for the desired value depends on the physicochemical classes of substances. To estimate the range of applicability of the proposed approach, let us consider using eq 3 for various homologue series. The coefficients of Antoine equation[2] were used as well as the data on the saturation pressure.[9,10] Our results are presented in Tables 1 to 7.

Conclusions

Table 8 presents the summary of the estimation’s error for the considered classes of liquids. One can clearly see that the deviation from the most reliable experimental data is not more than 2 %. The only exception is aliphatic alcohols and nitrogen compound substances, which contain the hydrogen bonds.

For this reason, we can conclude that proposed methods using eq 7 allow us to calculate the critical pressure for any nonpolar and weakly polar substances without the hydrogen bonds with the exactness comparable to an experimental error.

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