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The Critical Surface

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It is a widely unknown or unrecognized fact that the vapor−liquid critical points of pure compounds and also of mixtures form a sail-like surface in the three-dimensional space of temperature, pressure, and molar volume or density. The available experimental critical points of all pure compounds lie on or near that critical surface with some exceptions caused mainly by extraordinary intermolecular interactions (e.g., strong acids or polar compounds like water). For this surface and therefore the relation among the three critical properties, simple relation equations, transformable and explicit in each property, were evaluated and optimized. With these equations the critical volume, pressure, or temperature can be calculated from the two remaining properties with an average absolute deviation of less than 5 % over a set of recommended critical points for 421 organic compounds. This relation is also applicable for the critical properties of binary and multicomponent mixtures. Therefore, a unique tool is available for a consistency test of experimental or predicted data and for simple and reliable calculations of the often missing property, for example, the critical molar volume.

Introduction

The most unique state of a compound is the vapor−liquid critical point. The vapor−liquid critical temperature, pressure, and density or volume is decisive for the fluid phase behavior of the substance. According to the corresponding state principle proposed by van der Waals, most equations of state and many simpler correlations are based on the critical properties as parameters and/or reducing constants. Many papers and books are published about the critical phenomena, experimental techniques, and estimation methods for critical properties.[1−3] There are trends visible in the critical properties of homologous series corresponding to the molecular weight or other properties.[4] Some relations between normal boiling temperatures and critical temperatures of substances were published.[1] Young published in 1899[5] a relation between theoretical and observed critical density. Simple equations for calculating the critical pressure from the critical temperature and critical volume were published in 1942 by Meissner and Redding[6] and in 1990 by Grigoras.[7] The general applicability and relevance of this relation was not yet considered in these publications.

The need for a descriptive view of the three-dimensional (3D) $P\rho T$ surface became necessary during the Ph.D. thesis of the author, while working on the experimental determination of liquid and supercritical densities as a function of temperature and pressure.[8,9] Since the available standard software provided no simple solution to obtain a 3D view of the data points, a simple 3D plot software was developed. This software was combined with common spreadsheet software and therefore enabled a 3D view of arbitrary data points in a spreadsheet. Several years ago the author discovered that the experimental critical temperature, pressure, and molar volume or density of different compounds form a "sail shaped" surface in 3D space: the critical surface.

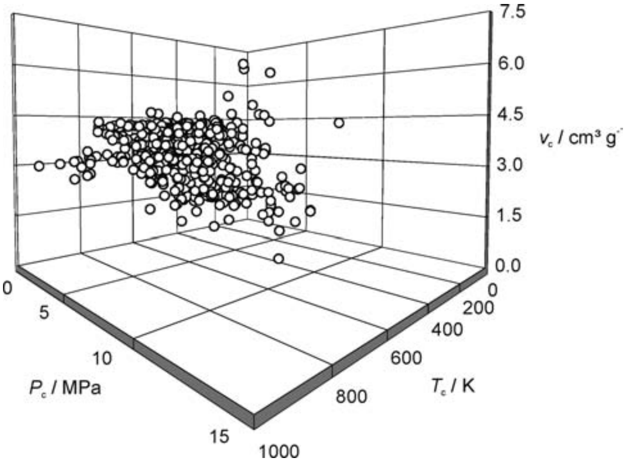

Figure 1. Critical points with critical temperature, pressure, and mass volume of 559 unselected pure compounds forming no significant macro structure.

Critical Surface Phenomenon

After plotting three columns with the critical temperatures, critical pressures, and critical mass volumes (or mass densities) of pure compounds, the resulting 3D view does not reveal any major structure as shown in Figure 1. However, by changing to the molar densities or volumes, the critical points are located on or near a surface in the 3D space as presented in Figure 2. That means that there is a direct general relation among the three critical properties of temperature, pressure, and molar volume.

The fact that not all critical points are exactly on one surface has different explanations. One reason is the high uncertainty of the experimental determinations of the critical properties. For most stable compounds very reliable measurements of critical temperatures and pressures with less than 0.1 K and 5 kPa deviations are possible at moderate conditions (e.g., up to 450

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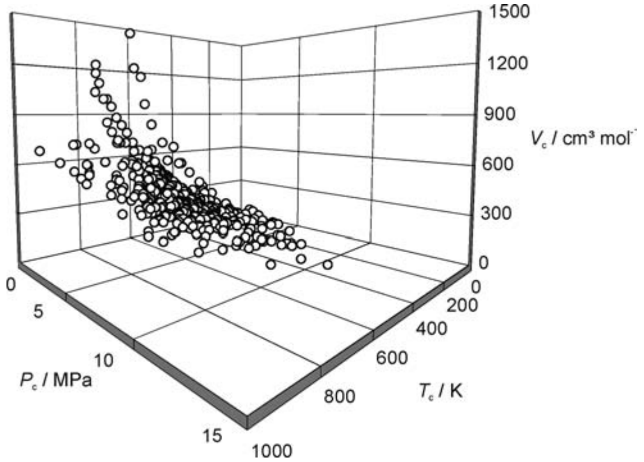

Figure 2. Critical points with critical temperature, pressure, and molar volume of 559 unselected pure compounds forming a surface in the 3D space: the critical surface.

K). It is more difficult to determine the critical volume or density, because of certain critical phenomena. Uncertainties of 1 % or more are typical for that property.[10] Furthermore there is the effect of impurities on the accuracy of the measurements. At higher temperatures the number of experimental critical data is limited and afflicted with increasing errors. This is also caused by the instability of numerous heavier compounds at their critical points. All of these effects reduce the number of substances with accurately determined critical points. Good and comprehensive reviews on all aspects about the critical point and experimental methods can be found in the papers of Kobe and Lynn,[11] Sengers,[12] and Ambrose and Young.[13]

Further crucial reasons for an offset of the critical point from the ideal surface are special intermolecular interactions as can be found for compounds with certain functional groups. For example, for alkanoic acids, methanol, or water, the experimental critical volumes (densities) are smaller (higher) than the values on the critical surface at their critical temperatures and pressures. This effect is caused by the stronger intermolecular interactions of the acid group or from hydrogen bonding. This results in smaller molar volumes than for similar compounds without these interactions. Consequently, the influence of the acid group decreases from formic acid to propanoic acid to the long-chain alkanoic acids. Therefore, for hexanoic acid with almost no offset, no significant effect on the critical properties is visible.

Critical Surface Equation

The main problem for an effective development of an equation for the critical surface was to find a data set with reliable critical data points. For the first 3D plot 559 critical points from the pure component basic property file of the Dortmund Data Bank (DDB)[14] were used. Unfortunately, these values were neither referenced nor evaluated systematically for reliability. Moreover, some predicted values were included. Currently, there are 511 referenced experimental critical points (temperature, pressure, and density or volume) available in the DDB for pure substances.

A data set with critical points of 421 organic compounds from a series of papers published between 1995 and 2009 by Ambrose, Tsonopoulos, Marsh, and other authors[15−24] was used as the basis for further studies. These papers contain peer-reviewed, recommended critical parameters derived from the available experimental data. For 421 compounds all three critical parameters are available in these papers. During the investigations the recommended data for three compounds (butane-1,3-diol,[25] tetraethylsilane,[26] and 1,1-dimethylpropyl ethyl ether[27]) were replaced by newer or more reliable experimental data. The list of all 421 compounds with the recommended or experimental critical data can be found in the Supporting Information (Table S1).

This final data set was used to evaluate equations for the critical surface as shown in Figure 3. Because of the requirements for further applications this equation had to be as simple as possible and also transformable to calculate every critical property from the two known input properties.

As mentioned above, equations for the relationship between the critical properties were published earlier by Young[5] (eq 1), by Meissner and Redding[6] (eq 2), and by Grigoras[7] (eq 3):

$$P_c = \frac{R}{3.77}\frac{T_c}{V_c} \tag{1}$$

$$P_c = \frac{2.08T_c}{(V_c - 8)} \tag{2}$$

$$P_c = 0.29 + 2.02\frac{T_c}{V_c} \tag{3}$$

with the critical pressure P_c, critical temperature T_c, critical molar volume V_c, and the ideal gas constant $R = 8.314472$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

These simple one- or two-parameter equations are easily transformable to be explicit in each property. After evaluating these and several different equations, the relationships in eqs 1 and 3 became most promising for further study. Equation 1 is a modification of the ideal gas law, the simplest relation among temperature, pressure, and volume. The other two equations are simple extensions of this first equation.

Equations 1 to 3 were tested and compared using the recommended critical parameters for all 421 compounds. The results are summarized in Table 1. Each critical property was estimated from the remaining two critical properties.

Grigoras as well as Meissner and Redding developed estimation methods from molecular structural approaches to calculate the critical temperatures and critical volumes of pure compounds using molecular surface areas and quantum mechanical calculations. Equations 2 and 3 were propagated by the authors for the calculation of the remaining critical pressure. Although Poling et al.[1] stated the estimation method by Grigoras is of poor accuracy for calculating the critical properties, the relation between the critical properties itself is impressive.

However, the oldest and simplest eq 1 from Young shows the best results for calculating the critical properties. Moreover, it should be mentioned that the number of available and reliable critical data was limited in 1899. Grigoras used a database of 137 critical points for his study.

A further evaluation of eq 1 showed no potential for real significant improvement by refitting the parameter using the currently available recommended critical points. Simplifying eq 1 by replacing quotient $R/3.77$ with an optimized constant results in the simple but reliable eq 4 that also has a slightly improved quality:

$$P_c = 2.2\frac{T_c}{V_c} \tag{4}$$

The critical relation constant 2.2 has the same unit as the ideal gas constant ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) and is only 0.2 % lower than the quotient $R/3.77$ suggested by Young.

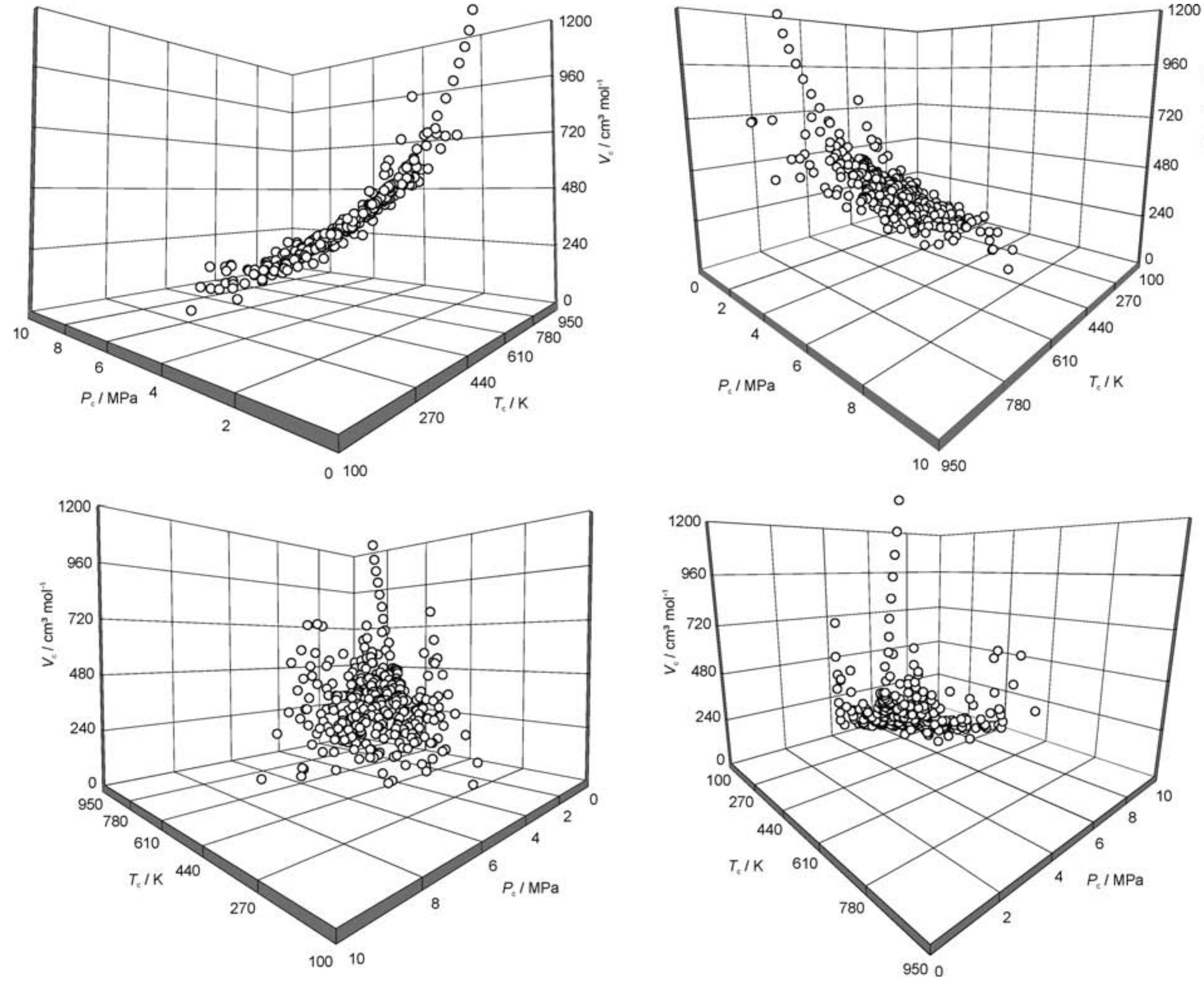

Figure 3. Recommended critical points of 421 pure compounds forming the surface in the 3D space: the critical surface (different 3D views).

Table 1. Summary of Calculated Critical Properties Using the Equations Published by Young[5] (eq 1), by Meissner and Redding[6] (eq 2), and by Grigoras[7] (eq 3) Compared to Recommended Critical Properties of 421 Pure Compounds

equation	1	2	3
AAD[a] (P_c)	4.70 %	8.64 %	6.05 %
AAD[a](V_c)	4.70 %	5.24 %	7.15 %
AAD[a](T_c)	4.41 %	9.40 %	6.25 %
Err (P_c)[b] > 10 %	40	141	66
Err (P_c)[c] < 5 %	309	90	260
Err (V_c)[b] > 10 %	40	46	78
Err (V_c)[c] < 5 %	309	269	241
Err (T_c)[b] > 10 %	43	170	75
Err (T_c)[c] < 5 %	308	83	244

[a] AAD is average absolute deviation in percent over all 421 compounds compared to the values in Table S1 of Supporting Information. [b] The number of substances for which the absolute percentage error is greater than 10 %. [c] The number of substances for which the absolute percentage error is less than 5 %.

Table 2. Summary of Calculated Critical Properties Using the Simple Critical Surface Equation 4 and the Optimized Two-Parameter Equation 5 Compared to Recommended Critical Properties of 421 Pure Compounds

equation	4	5
AAD[a] (P_c)	4.68 %	4.67 %
AAD[a] (V_c)	4.68 %	4.63 %
AAD[a] (T_c)	4.41 %	4.38 %
Err (P_c)[b] > 10 %	41	42
Err (P_c)[c] < 5 %	308	307
Err (V_c)[b] > 10 %	41	41
Err (V_c)[c] < 5 %	308	307
Err (T_c)[b] > 10 %	44	41
Err (T_c)[c] < 5 %	307	308

[a] AAD is average absolute deviation in percent over all 421 compounds compared to the values in Table S1 of Supporting Information. [b] The number of substances for which the absolute percentage error is greater than 10 %. [c] The number of substances for which the absolute percentage error is less than 5 %.

In a second step the two parameters of the also promising but less accurate eq 3 were refitted using the available database, which resulted in an optimized two-parameter critical surface equation:

$$P_c = -0.025 + 2.215\frac{T_c}{V_c} \tag{5}$$

The deviations from calculations using eqs 4 and 5 compared to the recommended critical parameters for all 421 compounds are summarized in Table 2. Each critical property was again estimated from the remaining two critical properties.

The optimized eqs 4 and 5 are applicable with similar reliability. The simple critical surface eqs 1 or 4 are easy to use and represent the ideal critical surface. In Figures 4 to 6 the calculated values using eq 4 are compared with the recommended data for the critical molar volume, temperature, and pressure.

All deviations were calculated using the full set of 421 data points including the already mentioned exceptions with higher deviations caused by special intermolecular interactions like

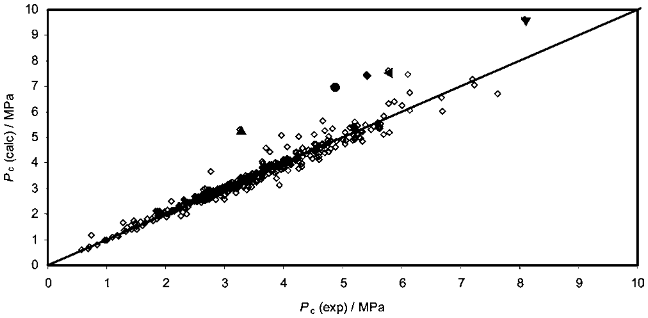

Figure 4. Comparisons of the experimental critical pressures of 421 pure components with calculated values using eq 4 and the recommended critical temperatures and molar volumes. Some compounds with higher deviations: ▲, trifluoroethanoic acid; ●, acetonitrile; ◆, hydrogen cyanide; left-pointing triangle, acetic acid; ▼, methanol.

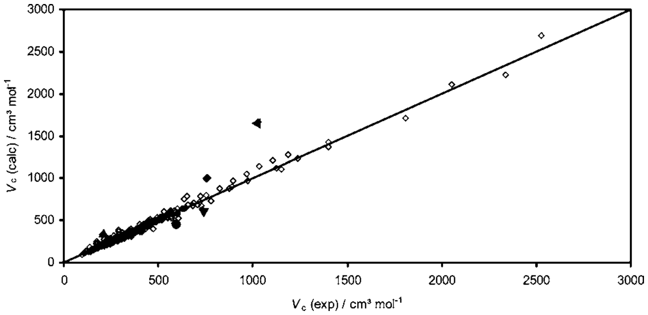

Figure 5. Comparisons of the experimental critical molar volumes of 421 pure components with calculated values using simple eq 4 and the recommended critical temperatures and pressures. Some compounds with higher deviations: ▲, trifluoroethanoic acid; ●, (1,1′-biphenyl)-2-amine (2-aminobiphenyl); ◆, dodecafluoroheptanaoic acid ethyl ester; left-pointing triangle, tetraoxaheptadecafluorononanoic acid.

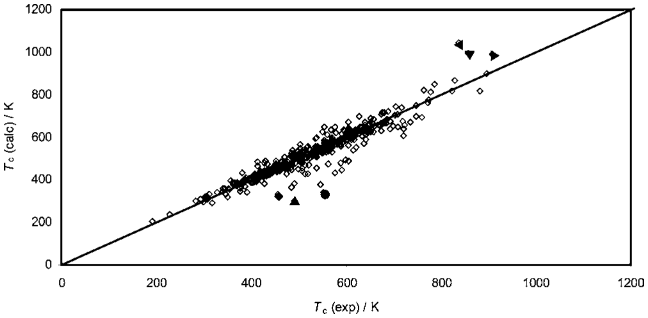

Figure 6. Comparisons of the experimental critical temperatures of 421 pure components with calculated values using eq 4 and the recommended critical pressures and molar volumes. Some compounds with higher deviations: ▲, trifluoroethanoic acid; ●, acetonitrile; ◆, hydrogen cyanide; left-pointing triangle, 2-aminobipheyl; right-pointing triangle, 1,1′:4′,1″-terphenyl (*p*-terphenyl); ▼, 1,1′:2′,1″-terphenyl (*o*-terphenyl).

methanol, acetic acid, propanoic acid, hydrogen cyanide, acetonitrile, propionitrile, trifluoroethanoic acid, and 2,4,6,8-tetraoxaheptadecafluorononanoic acid (all with smaller experimental molar volumes than the calculated values). When excluding only these eight compounds the absolute average deviations decrease from about 4.7 % to 4 % in volume and pressure for eq 4.

Some higher deviations are most probably caused by the uncertainties of the experimental data. For example the critical points of the terphenyl isomers show higher deviations. However, the critical temperatures of these compounds are between (857 and 908) K where accurate and reliable experimental determinations are very difficult. The calculated values using eq 4 and deviations from the recommended data for all 421 compounds are listed in Table S2 of the Supporting Information.

The range covered by the evaluation and optimization of eqs 1 to 5 reaches from $T = (190 \text{ to } 908)$ K, from $P = (0.57 \text{ to } 8.08)$ MPa, and from $V = (98.6 \text{ to } 2524)$ cm^3·mol^{-1} (in mass density: (163 to 870) kg·m^{-3}).

Critical Points of Pure Components

Equations 4 and 5 are evaluated and optimized using only critical data of organic compounds and therefore applicable with an uncertainty of less than 5 % for all organic compounds. Exceptions are small molecules with one or two carbon atoms (e.g., methane, methanol, ethanol) and molecules with strong intermolecular interactions (e.g., formic acid to pentanoic acid), where higher deviations of 10 % and more must be accepted. However, a considerable part of the deviations are caused by experimental uncertainties, which also result in a certain scattering of the experimental data. This can be seen from the comparisons for some siloxane compounds in Table 3 which were taken from the DDB.[14] The data of Flaningam[28] show higher deviations for all compounds than all other available experimental data even from older references. However, a scattering in the experimental data of about 5 % to 10 % can be assumed especially for heavier compounds with higher critical temperatures as can be seen for the shown siloxanes.

In addition to the 421 critical points used for the evaluation of the critical surface equations, the DDB contains critical points for about 200 further components including 29 elements and 27 inorganic compounds like hydrogen, nitrogen, arsenic, gold, hydrogen chloride, ammonia, sulfur dioxide, and so forth. For these inorganic compounds and elements the evaluated equations are not reliably applicable. Deviations of 20 % or more are typical for elements that have either very high critical temperatures (above 1000 K, e.g., for metals) or very low critical temperatures (below 200 K, e.g., for halogens) combined with high uncertainties in the experimental critical values or extraordinary intermolecular interactions. Exceptions are the sulfur oxides and the fluorides which are described very well. Details can be found in the Supporting Information (Table S3).

Despite the higher deviations from the critical equations, an extended critical surface can be anticipated in a 3D view of all available data at higher and lower temperatures. Unfortunately, the reliability and especially the number of available data for an extension of the determined critical surface to lower or higher temperatures are limited.

For water with a very high critical temperature and pressure and a very low critical volume of about 56 cm^2·mol^{-1} the deviations from eqs 4 and 5 are about 15 %.

Critical Points of Mixtures

After investigating the pure organic and inorganic components and elements, the question arose: are the critical points of mixtures also part of the discovered critical surface? The first tests confirmed the same reliability as for the pure compounds with some similar exceptions. Several mixture data are available for mixtures containing components like methanol that have much smaller critical volumes than estimated by the critical surface equations (same as for pure methanol). Therefore, mixtures containing these components also show higher deviations of 20 % or more for the critical molar volume.

However, the critical surface equations are quite reliable for mixtures of most organic components. Experimental critical points of several binary mixtures compared with predictions using the critical surface eq 4 are shown in Figures 7 to 11. For most evaluated systems like ethylene + methylamine (see Figure 7), benzene + butan-1-ol, benzene + propan1-ol, and benzene

Table 3. Experimental Critical Data of Siloxanes with Calculated Critical Molar Volumes Using Equation 4

T_c / K	p_c / MPa	$V_{c,exp}$ / $cm^3 \cdot mol^{-1}$	$V_{c,calc}$ / $cm^3 \cdot mol^{-1}$	deviation	source
Hexamethyldisiloxane [107-46-0], $M = 162.38\ g \cdot mol^{-1}$					
518.45	2.53	611	450.8	26.2 %	Flaningam (1986)[28]
518.8	1.91	633.3	597.6	5.6 %	McClure and Neville (1977)[29]
Octamethyltrisiloxane [107-51-7], $M = 236.53\ g \cdot mol^{-1}$					
564.35	1.723	868	720.6	17.0 %	Flaningam (1986)[28]
565.4	1.46	898.8	852.0	5.2 %	McClure and Neville (1977)[29]
564.13	1.415	881.8	877.1	0.5 %	Lindley and Hershey (1990)[30]
Octamethylcyclotetrasiloxane [556-67-2], $M = 296.62\ g \cdot mol^{-1}$					
587.35	1.824	970	708.4	27.0 %	Flaningam (1986)[28]
586.5	1.324	910	974.3	−7.1 %	Hicks and Young (1971)[26]
586.5	1.393	984	926.3	5.9 %	Young (1972)[31]
587	1.419	954	910.4	4.6 %	Osthoff and Grubb (1954)[32]
Decamethyltetrasiloxane [141-62-8], $M = 310.69\ g \cdot mol^{-1}$					
599.15	1.32	1157	998.6	13.7 %	Flaningam (1986)[28]
599.4	1.19	1212	1108.1	8.6 %	McClure and Neville (1977)[29]

+ ethanol (all Figure 8), acetonitril + butane (Figure 9), carbon dioxide + trifluoromethane and trifluoromethane + sulfur hexafluoride (both Figure 10), or butan-1-ol + methanol and butan-1-ol + diethyl ether (both Figure 11), deviations between experimental and calculated critical molar volumes are below 5 % with only a few exceptions. However, sometimes much higher deviations can be observed, for example, for the system ethylene + benzene (Figure 7) with deviations up to 26 %, which are maybe a result of higher uncertainties in the experimental data since these mixture values are not reviewed like the recommended critical properties for the pure compounds used in this work.

The critical points of multicomponent mixtures show that this general relation between the critical properties is valid. For the carbon dioxide rich mixture shown in Figure 12 eq 4 represents the critical volume with deviations of about 3 % to 6.5 %.

Applications of the Critical Surface Equation

The relation of the critical parameters that lead to the critical surface is of importance for various applications. The most

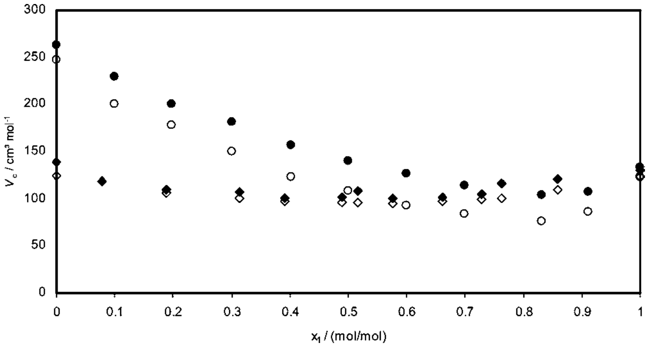

Figure 7. Comparisons of the experimental (solid symbols) and calculated (open symbols) critical molar volumes: ◆, ◇, ethylene (1) + methylamine (2) (experimental data from Li and Kiran[33]); ●, ○, ethylene (1) + benzene (2) (experimental data from Liu et al.[34]); calculated volumes using eq 4 and the experimental critical pressures and temperatures.

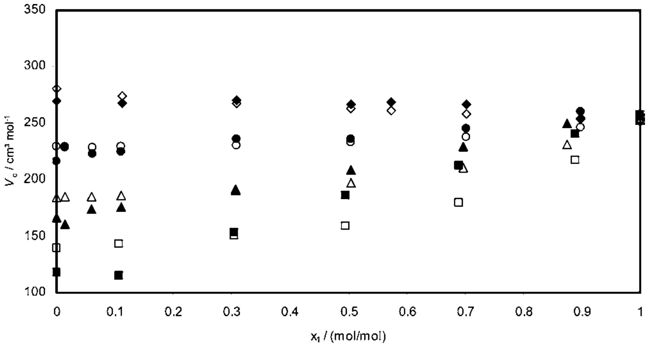

Figure 8. Comparisons of the experimental (solid symbols) and calculated (open symbols) critical molar volumes: ■, □, benzene (1) + methanol (2); ▲, △, benzene (1) + ethanol (2); ●, ○, benzene (1) + propan-1-ol (2); ◆,◇, benzene (1) + butan-1-ol (2); experimental data from Skaates and Kay[35] compared with calculated volumes using eq 4 and the experimental critical pressures and temperatures.

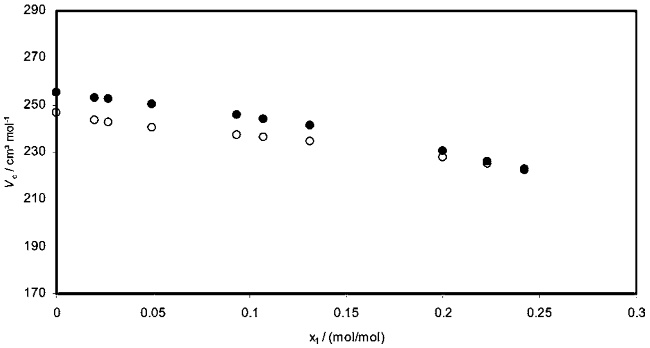

Figure 9. Comparisons of the experimental (solid symbols) and calculated (open symbols) critical molar volumes: ●, ○, acetonitrile (1) + butane (2); experimental data from Warowny[36] compared with calculated volumes using eq 4 and the experimental critical pressures and temperatures.

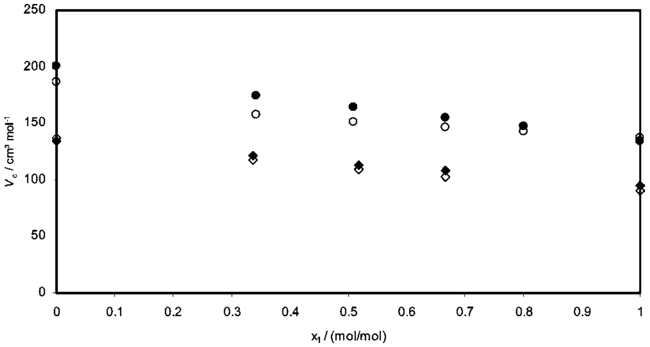

Figure 10. Comparisons of the experimental (solid symbols) and calculated (open symbols) critical molar volumes: ◆, ◇, carbon dioxide (1) + trifluoromethane (2) mixtures; ●, ○, trifluoromethane (1) + sulfur hexafluoride (2); experimental data from Diefenbacher et al.[37] compared with calculated volumes using eq 4 and the experimental critical pressures and temperatures.

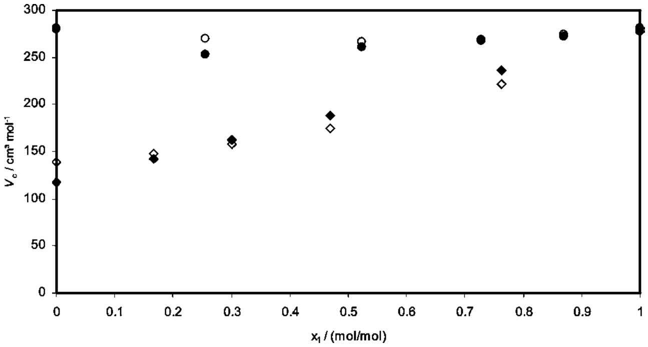

Figure 11. Comparisons of the experimental (solid symbols) and calculated (open symbols) critical molar volumes: ◆, ◇, butan-1-ol (1) + methanol (2); ●, ○, butan-1-ol (1) + diethyl ether (2); experimental data from Kay and Donham[38] compared with calculated volumes using eq 4 and the experimental critical pressures and temperatures.

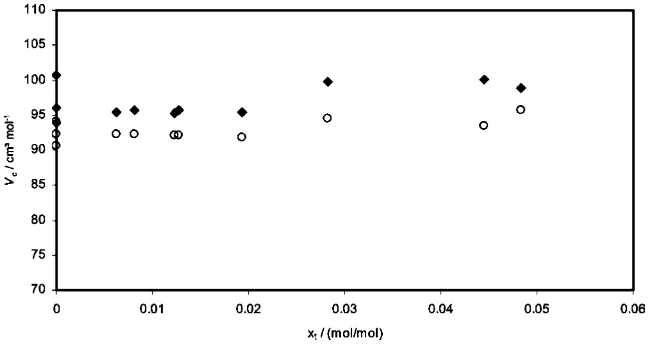

Figure 12. Comparisons of the experimental (solid symbols) and calculated (open symbols) critical molar volumes for a multi component system: ◆, ○, ethane (1) + propane (2) + butane (3) + carbon dioxide (4); experimental data from Morrison and Kincaid[39] compared with calculated volumes using eq 4 and the experimental critical pressures and temperatures.

obvious application is the calculation of a missing critical parameter from two available critical parameters. As mentioned above, the experimental determination of critical volumes or densities is more difficult and at the same time afflicted with higher uncertainties than the determination of critical temperatures and pressures. Therefore, the prediction of critical volumes from experimental critical temperatures and pressures is one of the most promising and relevant applications. Because of the high scattering in experimental critical volumes, the estimation of this property using a critical surface equation may be more reasonable than a questionable experimental determination for many applications.

Even if all three critical properties are available, the equations can be used for a quick consistency check of the experimental investigations or questionable literature data prior to its usage in further calculations.

For consistency tests of critical properties, to calculate missing properties, and to provide an alternative critical density for Helmholtz energy equations of state, eq 5 is already implemented in the thermodynamic correlation and calculation software DynaSol ThermoProp.[40]

Sometimes the critical properties are not experimentally available because of the instability of the molecule or mixture or the capability of the experimental equipment. Different estimation methods based mostly on the group contribution principle become useful as those stated by Daubert.[41] In the DDB 10 or more different published estimation methods are implemented. However, these prediction methods are separate and independent. Some methods are limited to certain groups, for example, hydrocarbons.[2] These methods are always based on the available experimental data; therefore, the same limitations and problems can be found. Again the critical volume is the property with the highest uncertainty, but there is an increasing need for this property especially for equation of state development. The derived critical surface equation combined with estimation methods for the critical temperature and pressure is a simple solution to eliminate this problem or to verify estimated properties. Moreover, the estimation methods for the critical volume often show higher uncertainties than the critical surface equations.

Conclusions

The vapor−liquid critical points determined by the critical temperature, critical pressure, and critical molar volume or density of almost all compounds form a critical surface in the 3D space. By evaluating several hundred experimental or derived recommended critical points of pure organic compounds, simple equations for this critical surface were evaluated and optimized. These critical surface equations are easily convertible to be explicit in all three properties. The equations are applicable for almost all organic and many inorganic compounds with an average uncertainty of less than 5 % over the available critical data. Exceptions with higher deviations are small molecules (e.g., methane) and molecules with strong intermolecular interactions like acetic acid. Moreover, the equations can be used for mixtures of organic compounds. The critical surface phenomenon and the derived equations lead to numerous applications for consistency tests or the prediction of missing critical parameters.

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Supporting Information Available:

Tables S1 to S3 contain the used reference critical data (Table S1) from the literature,[15−24] the deviations using eq 4 (Table S2), and deviations of calculated critical data using eq 4 to various experimental critical data for inorganic components and elements (Table S3) from the DDB.[14] This material is available free of charge via the Internet at http://pubs.acs.org.

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