Critical Constants Correlation from van der Waals Equation

Mario Alberto Martínez-Vitela[1] and Jesús Gracia-Fadrique[2]

Abstract

The cubic van der Waals equation of state at the critical condition is reduced to a linear function (V_c vs. T_c/P_c coordinates) with one adjustable parameter. It is shown that at the critical point the relation $V_c = 3V_o$ must not hold as van der Waals suggested, but the attractive constant $\alpha = P_c V_c^2$ remains. Selected values of T_c, P_c, V_c compiled by Ihmels where focused on testing the quality of several empirical equations relating critical conditions. It is shown that the obtained critical constants correlation is a general form of the empirical expressions proposed by Young, Meissner, Bird, Grigoras and Ihmels. From the resulting correlation function, a function for the critical compressibility is proposed. The critical volume V_c and the ratio T_c/P_c have been expressed in group contributions.

Keywords: Van der Waals; critical point; equation of state; empirical correlations; group contributions.

---

[1] Facultad de Química, Universidad Nacional Autónoma de México, mario.vitela@gmail.com, ORCID:0000-0003-0553-2113, Ciudad de México, México.
[2] Facultad de Química, Universidad Nacional Autónoma de México, jgraciaf@unam.mx, ORCID:0000-0003-0553-2113, Ciudad de México, México.

Correlación de constantes críticas a partir de la ecuación de van der Waals

Resumen

La ecuación de estado cúbica de van der Waals en la condición crítica se reduce a una función lineal (en coordenadas V_c frente a T_c/P_c) con un parámetro de ajuste. Se muestra que en el punto crítico, la constante $V_c = 3V_o$ debe efectivamente descartarse como hizo van der Waals, no así con la constante atractiva $\alpha = P_c V_c^2$. Los valores seleccionados de T_c, P_c, V_c compilados por Ihmels se enfocaron en probar la calidad de varias ecuaciones empíricas renombradas que relacionan condiciones críticas. En este artículo se muestra que la correlación de constantes crítica obtenida es una forma general de estas expresiones empíricas propuestas por Young, Meissner, Bird, Grigoras e Ihmels. Se propone una función para la compresibilidad crítica, única por familia homóloga. El volumen crítico V_c y la relación T_c/P_c se expresa en función de contribución de grupos.

Palabras clave: Van der Waals; punto crítico; ecuación de estado; correlaciones empíricas; contribuciones por grupo.

1   Introduction

The critical point is a thermodynamical state that represents the end of the coexistence line between different phases. At the vapor-liquid equilibrium, the difference in density between the liquid and vapor becomes zero at the critical point, the meniscus between the two phases disappears, latent heat of vaporization goes to zero, the refraction index is the same for both phases, and the interfacial tension is zero. The critical point establishes the coordinates of the critical temperature, critical pressure, and critical volume, which define one of the essential physicochemical parameters, the critical compressibility factor Z_c.

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

where P_c is the critical pressure, V_c is the critical molar volume, T_c is the critical temperature, and R is the gas constant. The principle of corresponding states expects a unique and constant value of Z_c for all substances, and van der Waals in his famous doctoral thesis predicts a

universal value of Z_c, being $Z_c = 3/8$. However, it is widely known that Z_c is not constant and, furthermore, the critical data shows that the value of Z_c is rather far from the prediction of $3/8$. In general, equations of state fail to predict the critical properties, and the use of critical exponents to describe changes of density, surface tension, heat of vaporization is a widely employed tool. Guggenheim in his seminal work [1] pointed out the universality of critical exponents.

In the time lapse between van der Waals doctoral thesis in 1873 [2] and his lecture of the physics Nobel Prize in 1910, there was an increased number of critical measured data. Sydney Young [3] provided one of the first high-quality critical data series, and van der Waals refers to them in order to correct the value of Z_c:

"Sydney Young determines inter alia the value of PV/RT at the critical point and finds $1/3.77$. If P and T have the same values as in my theory, providing b is imagined to be constant, the difference from $3/8$, the value which I found for PV/RT, can be ascribed wholly to the volume. And this, we can say, is entirely correct. The critical volume is not $3b$... ...And the product PV/RT is not $3/8$ but $3/8\sqrt{2}$" [4].

As van der Waals himself adverts, the insufficiency of his equation evaluating the critical volume promotes the search for equations able to calculate the critical volume.

The construction of theories and models able to describe thermodynamical properties near the critical region is an ongoing field. Velasco *et al.* [5] represent the critical behavior with a theory of renormalization of groups and warn that consistency problems arise from the vapor pressure and propose an equation to describe the critical point. Li *et al.* [6] proposed a correlation for the prediction of critical properties for 16 homologous families using molecular descriptors and focused on the critical temperature. Mersmann and Kind [7] can predict among other properties the critical molar volume proposing a correlation based on the corresponding states principle, using the atomic radii and an empirical factor for several homologous series with an acceptable error.

Several semiempirical correlations are based on the relations between critical properties, according to the principle of corresponding states. Correlations near the critical point predict the behavior of substances at con-

ditions where experimental data is scarce, and they are useful to assert the quality of existing data. The critical temperature and pressure are intensive variables and they are easier to obtain than the critical volume, due to the strong fluctuations in density near the critical point, therefore the need of correlations able to predict the critical volume. Cailletet and Mathias were pioneers determining the critical density of several substances successfully. Together, Cailletet and Mathias developed an apparatus that allowed them to measure the density of saturated vapor and liquid phases. They have observed that the density linearly decreases for both phases when approaching the critical point. Consequently, they have enunciated the law of rectilinear diameters [8], an analytical function still valid and used as a comparison for other methods.

Ihmels [9] published selected data, which are presented in critical coordinates of temperature, volume and pressure. Ihmels found a random surface and noticed that when the volume is replaced by the molar volume, the data can be contained in a sail-like surface. Ihmels uses the critical data to qualify the empirical correlations of Young (Equation (2)) [3], Meissner-Redding (Equation (3)) [10], Bird (Equation (4)) [11], and Grigoras (Equation (5)) [12]. Ihmels proposes an optimized expression (Equation (6)) [9]

$$V_c = \frac{R}{3.77} \frac{T_c}{P_c} \tag{2}$$

$$V_c = 8 + 2.08 \frac{T_c}{P_c} \tag{3}$$

$$V_c = 2.02 \frac{T_c}{P_c + 0.29} \tag{4}$$

$$V_c = 2.17 \frac{T_c}{P_c - 0.29} \tag{5}$$

$$V_c = 2.215 \frac{T_c}{P_c + 0.025} \tag{6}$$

where V_c is the critical molar volume measured in cm^3/mol, T_c is the critical temperature measured in K, P_c is the critical pressure measured in

MPa, and R is the ideal gas constant $R =$8.3144598 MPa cm^3/mol K [13]. The constant with a value of 8 in Equation (3) has units of molar volume (cm^3/mol). The constants 2.08, 2.02, 2.17 and 2.215 in Equations (3) to (6) have units of MPa cm^3/mol K. In Equations (4) to (6), the constants 0.29, -0.29 and 0.0025 have units of pressure (MPa).

In this article we demonstrate that the above empirical equations, published in the literature since 1899 [3],[14],[15],[16] and of current use for the estimation of critical constants, are naturally derived from the van der Waals equation of state at the critical condition.

2 The van der Waals equation at the critical condition

Johannes Diderik van der Waals proposed in 1873 [2] the famous equation of state that provides an adequate approach of phase coexistence and its relation to the critical point. Despite the lack of accuracy on representing the thermodynamical properties in the vicinity of the critical point, the van der Waals equation describes qualitatively gas behavior, liquid-vapor transition, the liquid phase, as well as that of stable states, metastable states, and the critical point. The usual form of the van der Waals equation of state reads:

$$P = \frac{RT}{V - V_0} - \frac{\alpha}{V^2} \tag{7}$$

where V_0 is a parameter that has units of molar volume, initially associated with the concept of a covolume. However, V_0 is negative at low temperatures and changes sign at high temperatures, therefore it cannot be interpreted as the volume occupied by the molecules [17].

The van der Waals equation at the critical condition is given by

$$P_c = \frac{RT_c}{V_c - V_0} - \frac{\alpha}{V_c^2} \tag{8}$$

The critical condition, in terms of the principle of continuity of the gaseous and liquid phases, can be written as:

$$(V - V_c)^3 = 0 \tag{9}$$

Expanding Equation (9)

$$V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0 \tag{10}$$

The usual cubic structure of the van der Waals equation is [18]

$$V^3 - \left(V_0 + \frac{RT_c}{P_c}\right) V^2 + \frac{\alpha}{P_c} V - \frac{\alpha V_0}{P_c} = 0 \tag{11}$$

Equating the coefficients for the quadratic term V^2 in Equations (10) and (11)

$$3V_c = V_0 + \frac{RT_c}{P_c} \tag{12}$$

$$V_c = \frac{V_0}{3} + \frac{R}{3}\left(\frac{T_c}{P_c}\right) \tag{13}$$

From the coefficients for the linear term V in Equations (10) and (11)

$$3V_c^2 = \frac{\alpha}{P_c} \tag{14}$$

Substituing $\alpha = 3P_c V_c^2$ in Equation (8) gives

$$P_c = \frac{RT_c}{V_c - V_0} - 3P_c \tag{15}$$

Equation (15) explicit in the critical volume is

$$V_c = V_0 + \frac{R}{4}\left(\frac{T_c}{P_c}\right) \tag{16}$$

All these expressions are equally valid in the van der Waals context. Neglecting $V_c = 3V_0$, as van der Waals did in his Nobel Prize lecture [4] leaves two proposals for the relation V_c vs. T_c/P_c, Equations (13) and (16). Experimental data shows that Equation (16) is consistent as shown in section 3.2 Critical properties of homologous series and therefore the term $\alpha = 3P_c V_c^2$ is appropriate and quantitative at the critical point. The

intercept that substitutes $V_c = 3V_0$ is interpreted in the section 3.3 The meaning and content of V_0.

Equation (16) constitutes the fundamental expression to demonstrate that the previously discussed empirical correlations are a consequence of the van der Waals equation. The next section contains a comparison with each of the proposed correlations and the relation with the expressions of the critical compressibility factor.

3 Results

3.1 The empirical correlations

The volume-explicit expressions of Young (Equation (2)) and Meissner-Redding (Equation (3)) are obtained from Equation (16). When V_0 approaches zero, Equation (16) takes the form of the empirical correlation of Young (Equation (2))

$$V_c = \frac{R}{4}\left(\frac{T_c}{P_c}\right) \tag{17}$$

where $R/4$ is 5% lower than the empirical term $R/3.77$ suggested by Young.

The Meissner-Redding correlation (Equation (3)) is generated by Equation (16) with $R = 8.3144598$ MPa cm^3/ mol K. Note that $R/4$ in Equation (16) equals 2.0785, 2.08 in equation of Meissner-Redding (3), and the only adjustable parameter is V_0

$$V_c = V_0 + 2.0785\left(\frac{T_c}{P_c}\right) \tag{18}$$

The volume-explicit expressions of Bird (Equation (4)), Grigoras (Equation (5)) and Ihmels (Equation (6)) are obtained from Equation (16) when $V_0 = 0$ and $R = 8.3144598$ MPa cm^3/ mol K, therefore $R/4 = 2.0785$ MPa cm^3/ mol K. The structure of equations (4), (5) and (6) is similar, the variation of their constants reflect the increasing available critical

data. According to the critical properties selected by Ihmels, Equation (6) best fits the majority of critical data. Nevertheless, $P_c >> 0.025$, i.e., the pressure-related constant does not represent a significant adjustment to the critical properties, so these expressions can be written as

$$V_c = \frac{R}{4}\frac{T_c}{P_c} \tag{19}$$

$$V_c = 2.0785\frac{T_c}{P_c} \tag{20}$$

The slope $R/4 = 2.0785$ MPa cm^3/ mol K,substitutes the empirical slopes of 2.02 in Bird's Equation (4), 2.17 of Grigoras (5) and 2.186 of Ihmels (6).

3.2 Critical properties of homologous series

The critical properties of homologous series of organic compounds and some elements were tested under Equation (16), the results are shown in Figure 1. The obtained slope corresponds to the term $R/4$. If $R =8.3144598$ MPa cm^3/ mol K, then $R/4 =2.0785$. The slope remains practically constant for the tested families and in agreement with the expected $R/4$ value (2.065 $\pm$ 0.093) and the intercept V_0 is the only fitting parameter. The reported error is obtained by the quotient σ/n, where σ is the standard deviation and n the number of data.

Figures 1a and 1b show the variable T_c/P_c as a function of V_c for the n-alkanes and n-alkenes, respectively. Both homologous series show a linear behavior and obey Equation (23). The slope $R/4$ is reached, being 2.10 for the alkanes, and 2.03 for alkenes. The fitting parameter V_0 equals 18 for the n-alkanes and 32 for n-alkenes.

The value of V_0 predicted for the alcohols (Figure 1c) is negative, as well as in the carboxylic acids (Figure 1d). Water has been included as a reference for both series. These two series represent hydrogen bonds-forming molecules, leading to an increase in the intermolecular interactions, therefore when V_0 is negative and represents the dominance of attractive interactions. For the carboxylic acids, V_0 is approximately twice the value

than that of the alcohols, fact that can be interpreted as the increment of the hydrogen bond provided by the O-OH group present in the acids, that forms double the bonds than the OH group in the alcohols. Figure 1f contains the linear regression for elements. An analysis with confidence bands (0.999) shows that the intercept withholds no significance to the linear regression.

(a)

(b)

(c)

(d)

(e)

(f)
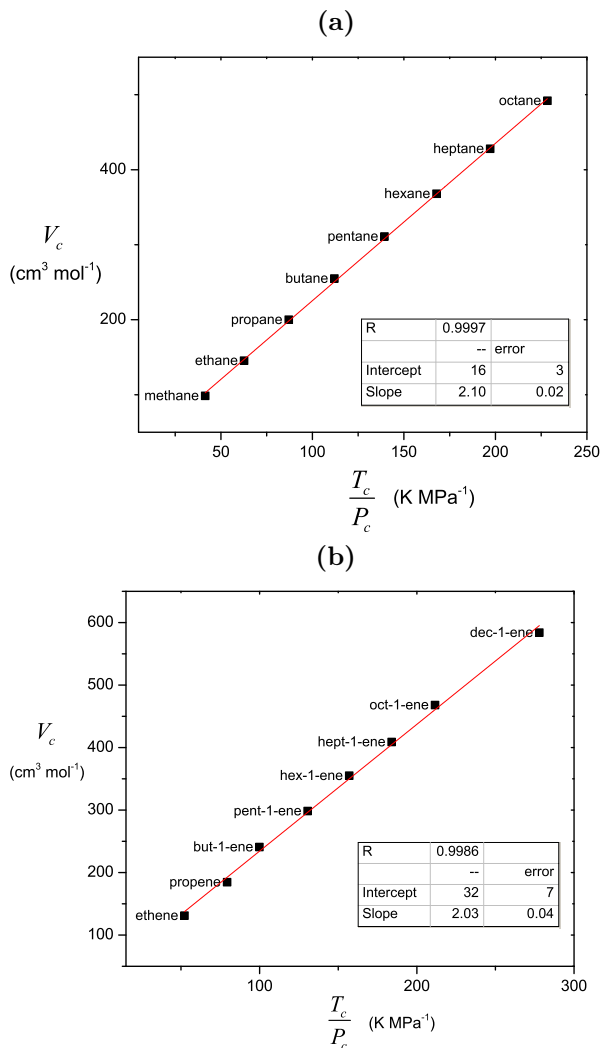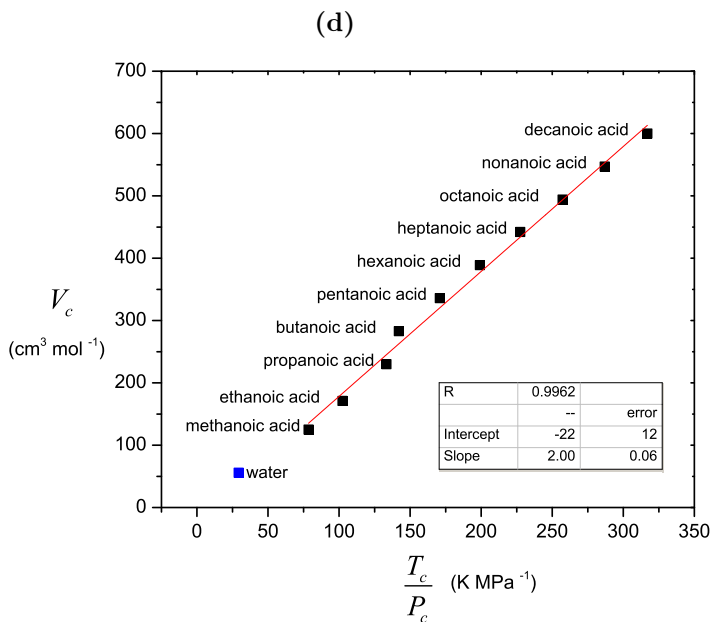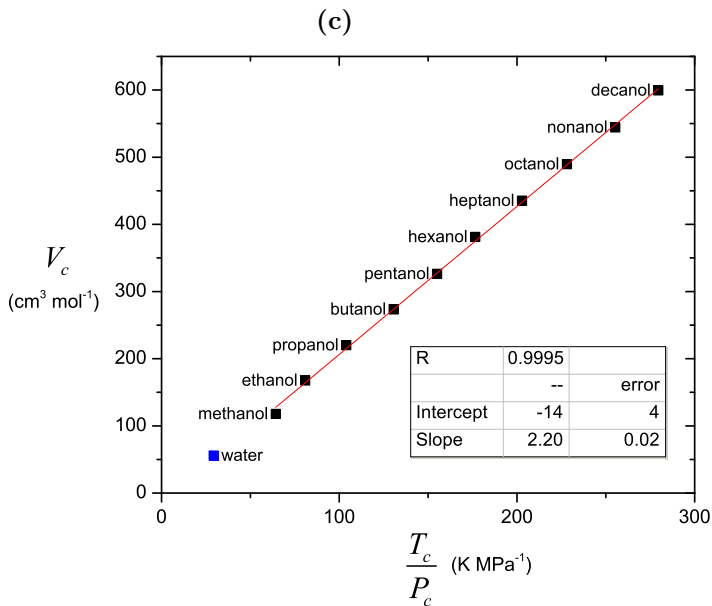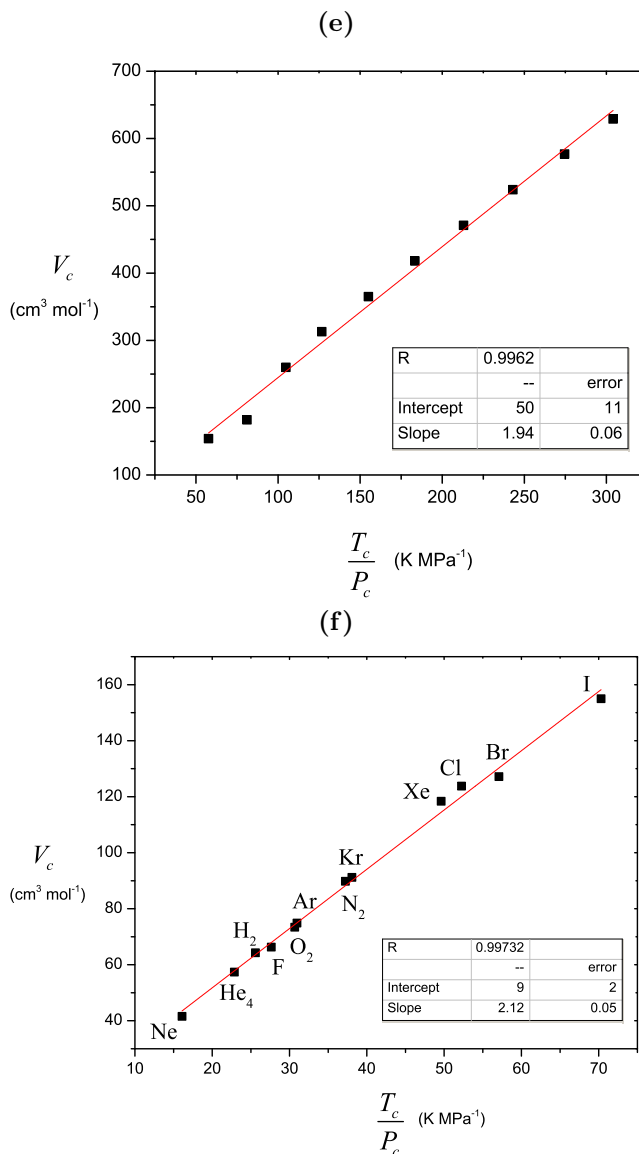
Figure 1: Critical volume V_c as a function of the ratio T_c/P_c for homologous series and some elements, Equation (16) with adjustable slope and intercept. (a) C1-C8 n-alkanes (b) C2-C10 n-alkenes (c) C1-C10 n-alcohols (d) C1-C10 carboxylic acids (e) C1-C10 primary n-amines (f) Elements. Data acquired from Yaws [19] Water added as reference.

3.3   The meaning and content of V_o

As it is expected, the critical molar volume in a homologous series shows a linear increment with the increment in carbon units, so the corresponding slope represents an additive and constitutive property. For example, in the alcohols homologous series:

$$V_c = V_c^* + m_1 n_c \tag{21}$$

where V_c^* represents the intercept and m_1 the corresponding slope or contribution for each -CH_2- group added to the molecule. The same behavior occurs with the quotient T_c/P_c; for the alcohols:

$$\frac{T_c}{P_c} = \left(\frac{T_c}{P_c}\right)^* + m_2 n_c \tag{22}$$

$(T_c/P_c)^*$ is the intercept and m_2 is the slope. The relation between both slopes is

$$m_1 = \frac{R}{4} m_2 \tag{23}$$

The difference of the Equation (21) and (22) with $R/4$ times the Equation (22), is

$$V_c - \frac{R}{4}\left(\frac{T_c}{P_c}\right) = V_c^* - \frac{R}{4}\frac{T_c}{P_c}^* = V_0 \tag{24}$$

that corresponds to the fundamental Equation (16). The same result is obtained by substracting the term $m_1 n_c$ in both sides of Equation (16). V_c^* and $(T_c/P_c)^*$ represents the non-hydrocarbon group contribution to each property (the hydrofilic portion for alcohols and carboxylic acids) of the molecule, its difference (Equation (24)) represents the value and sign of V_0 in Equation (16).

The evident linear relationship between T_c/P_c and V_c with respect to the number of carbon atoms n_c in a homologous series, as shown in Figure 2, allows the extrapolation for the estimation of critical properties. Note that the slope in V_c is practically double the slope in T_c/P_c.

(a)

(b)
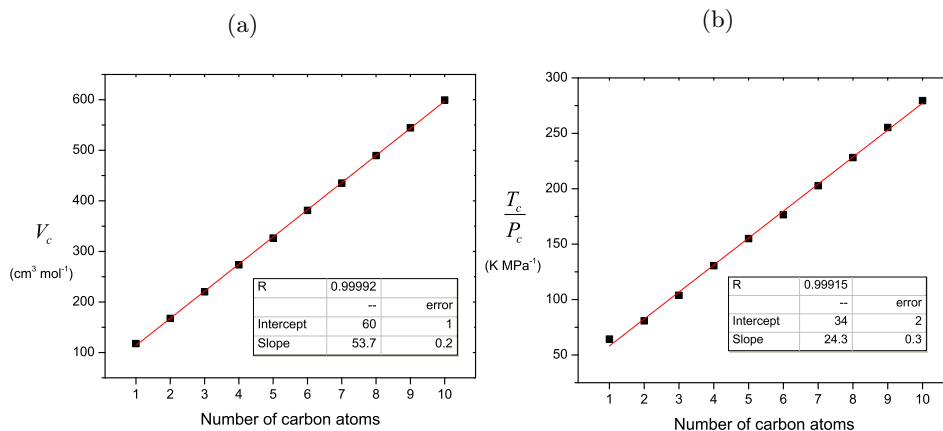
Figure 2: (a) V_c and (b) T_c/P_c as a function of the number of carbon atoms in n-alcohols series. [19]

The critical molar volume of a missing member in a homologous series can be predicted interpolating or extrapolating Equation (16). This represents a major advantage since the direct measurement of molar volume is very difficult due to the fact that, near the critical region, small changes in pressure produce large changes in density. The determination of critical molar volumes by this method constitutes a simple and convenient alternative to the experimental evaluation and the law of rectilinear diameter proposed by Cailletet and Mathias [8].

Equation (16) is useful when it is necessary to extrapolate or interpolate critical constants of compounds. Clear examples of compounds with few or no experimental data at critical conditions are polymers, proteins, surfactants and ionic liquids, due to the low vapor pressures and the high temperatures needed to reach the critical point [20].

The Equation (16) can lose sensibility when the values of critical constants are too close to each other, as in the case of isomers of hydrocarbons. In order to obtain an expression able to represent such families, the Equation (16) can be expressed as a function of the critical compressibility factor Z_c

$$Z_c = Z_c \frac{V_0}{V_c} + \frac{1}{4} \tag{25}$$

$$V_0 = V_c \left(1 - \frac{1}{4Z_c} \right) \tag{26}$$

$$V_0 = V_c - \frac{V_c}{4} \frac{1}{Z_c} \tag{27}$$

The proposed correlation is generalized by Equation (27) as a function of the critical molar volume V_c and the critical compressibility factor Z_c note that matches Equation (24). The critical compressibility factor usually ranges between 0.23 and 0.31 for most pure liquids [21]. Figure 3 shows the parameter V_0 as a function of the inverse critical compressibility factor Z_c according to Equation (27) for different series, where the critical properties are too similar.

According to Equation (27), when the critical compressibility factor tends to 0.25, V_0 tends to zero. If Z_c is lesser than 0.25, $V_0 < 0$ and in the case of Z_c being greater than 0.25, $V_0 > 0$. When Z_c takes the classical van der Waals value of $3/8$, the critical molar volume is $V_c = 3V_0$

$$Z_c = 0.25 \Rightarrow V_0 = 0$$

$$Z_c > 0.25 \Rightarrow V_0 > 0$$

$$Z_c < 0.25 \Rightarrow V_0 < 0$$
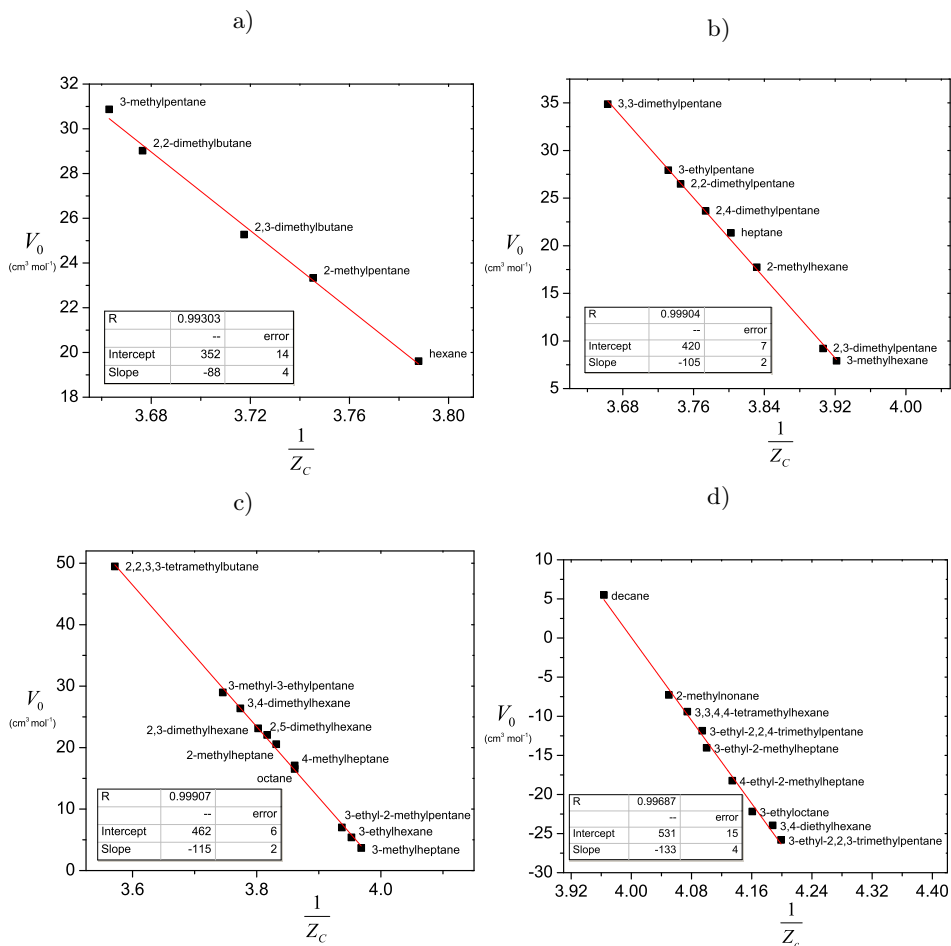
Figure 3: The parameter V_0 as a function of the critical compressibility factor Z_c for isomers, Equation (27) (a) Hexane (b) Heptane (c) Octane (d) Decane. Data acquired from Yaws [19]

ing.cienc., vol. 15, no. 30, pp. 81–99, julio-diciembre. 2019.

95|

Figure 4 shows an example of halide compounds with Z_c close to 0.25. Note that the intercept is fixed to zero, the slope is equivalent to $R/4$, and the correlation coefficient is close to 1.
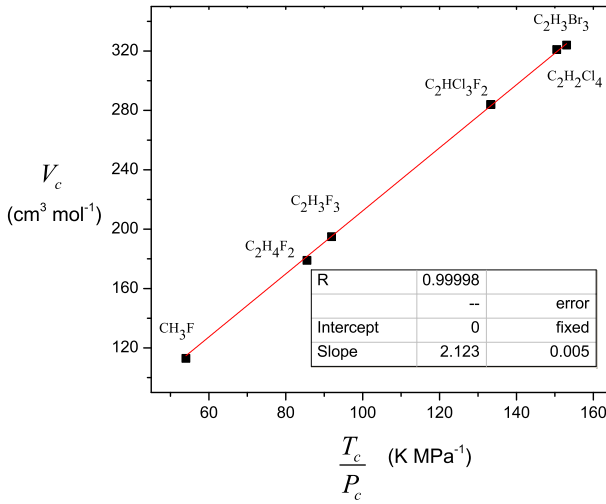
Figure 4: Critical volume V_c as a function of the ratio T_c/P_c for halide compounds with Z_c close to 0.25, Equation (16) with adjustable slope and intercept fixed to zero.

Equation (16) can be written as:

$$Z_c = Z_0 + \frac{1}{4} \tag{28}$$

where $Z_0 = P_c V_0 / R T_c$ is called pseudo compressibility factor. Equation (28) constitutes a function to represent the compressibility factor of homologous series. Concerning the values of V_0 and α van der Waals stated that he "never expected this equation, with a and b assigned a constant value, to give results numerically in agreement with experiment and yet people almost always act as though that were my opinion. This astonishes me as in my treatise of 1873 not only did I expressly emphasize the variability of b but also quoted a series of b-values from Andrews' experiment in which for small volumes the change in b with the volume is calculated." [4]

4   Conclusions

The van der Waals equation at the critical condition is reduced to a linear equation with one fitting parameter V_0. The critical constants correlation is valid for van der Waals fluids. This linear function represents different homologous series and groups of substances with similar molecular interactions when it is expressed in V_c vs. T_c/P_c coordinates. The exposed method constitutes a convenient tool for the quality assessment of experimental data and theoretical predictions near the critical region.

The critical correlation from van der Waals equation defines a function for the compressibility factor, according to the principle of corresponding states where Z_0 is a pseudo-compressibility factor. The equation explicit in the critical molar volume (Equation (16)) is a more convenient expression than the version explicit in the compressibility coefficient (Equation (28)) since it avoids the propagation of errors created by the product and quotient of the critical constants.

The critical correlation from van der Waals equation entails and improves the Young, Meissner, Bird, Grigoras and Ihmels empirical equations, commonly used in the correlation of critical properties frequently cited in textbooks and handbooks. Several empirical expressions that relate critical constants are naturally contained and based on the van der Waals equation at the critical condition.

Acknowledgements

References

[1] E. A. Guggenheim, "The principle of corresponding states," *The Journal of Chemical Physics*, vol. 13, pp. 253–261, 1945. [Online]. Available: https://doi.org/10.1063/1.1724033 83

[2] J. D. van der Waals, "Over de continuiteit van den gasen vloeistoftoestand," Ph.D. dissertation, Leiden, A,W, Sijthoff, 1873. [Online]. Available: https://trove.nla.gov.au/work/31662501 83, 85

[3] S. Young, "On the law of cailletet and mathias and the critical density," *Proc. Phys. Soc., London*, 1899. 83, 84, 85

[4] J. D. van der Waals. (1912, December) The equation of state for gases and liquids. The Nobel Prize Organisation. [Online]. Available: shorturl.at/uxGR2 83, 86, 96

[5] S. Velasco, M. J. Santos, and J. A. White, "Consistency of vapor pressure equations at the critical point," *Industrial & Engineering Chemistry Research*, vol. 54, pp. 12 993–12 998, 2015. [Online]. Available: https://doi.org/10.1021/acs.iecr.5b03577 83

[6] Z. Li, L. Zuo, W. Wu, and L. Chen, "The new method for correlation and prediction of thermophysical properties of fluids. critical temperature," *Journal of Chemical and Engineering Data*, vol. 62, no. 11, pp. 3723–3731, 2017. [Online]. Available: https://doi.org/10.1021/acs.jced.7b00454 83

[7] A. Mersmann and M. Kind, "Prediction of mechanical and thermal properties of pure liquids, of critical data, and of vapor pressure," *Industrial & Engineering Chemistry Research*, vol. 56, pp. 1633–1645, 2017. [Online]. Available: https://pubs.acs.org/doi/pdf/10.1021/acs.iecr.6b04323 83

[8] Cailletet and Mathias, "Recherches sur les densites des gaz liquefies et de leurs vapeurs saturees," *Journal de Physique Theorique et Appliquee*, vol. 5, pp. 549–564, 1886. [Online]. Available: https://doi.org/10.1051/jphystap:018860050054900 84, 93

[9] E. C. Ihmels, "The critical surface," *Journal of Chemical and Engineering Data*, vol. 55, no. 9, pp. 3474–3480, 2010. [Online]. Available: http://dx.doi.org/10.1021/je100167w 84

[10] H. P. Meissner and E. M. Redding, "Prediction of critical constants," *Industrial and Engineering Chemistry*, vol. 34, no. 5, pp. 521–526, 1942. [Online]. Available: http://dx.doi.org/10.1021/ie50389a003 84

[11] R. B. Bird, J. O. Hirschfelder, and C. Curtiss, "Molecular theory of gases and liquids," *Trans. Am. Soc. Mech. Eng.*, vol. 76, p. 1011, 1954. 84

[12] S. Grigoras, "A structural approach to calculate physical properties of pure organic substances: The critical temperature, critical volume and related properties," *Journal of Computational Chemistry*, vol. 11, pp. 493–510, 1990. [Online]. Available: https://doi.org/10.1002/jcc.540110408 84

[13] P. J. Mohr, D. B. Newell, and B. N. Taylor, "Codata recommended values of the fundamental physical constants: 2014," *Rev. Mod. Phys.*, vol. 88, p. 035009, 2016. [Online]. Available: https://link.aps.org/doi/10.1103/RevModPhys.88.035009 85

[14] K. A. Kobe and R. E. Lynn, "The critical properties of elements and compounds." *Chemical Reviews*, vol. 52, no. 1, pp. 117–236, 1953. [Online]. Available: http://dx.doi.org/10.1021/cr60161a003 85

[15] J. A. Riddick, W. B. Bunger, and T. K. Sakano, *Organic Solvents: Physical Properties and Methods of Purification.* Wiley, 1986. 85

[16] B. E. Poling, J. M. Prausnitz, and J. P. OConnell, *The Properties of Gases and Liquids*, 5th ed. McGraw Hill, 2004. 85

[17] K. Denbigh, *The principles of Chemical Equilibrium.* Cambridge, UK: Cambridge University., 1971. 85

[18] S. M. Walas, *Phase Equilibria in Chemical Engineering.* Butterworth-Heinemann, 1985. 86

[19] C. L. Yaws, *Chemical properties handbook: physical, thermodynamics, enviromental, transport, safety, and health related properties for organic and inorganic materials.* McGraw-Hill, 1999. 91, 93, 95

[20] J. O. Valderrama and R. E. Rojas, "Critical properties of ionic liquids. revisited," *Industrial and Engineering Chemistry Research*, vol. 48, no. 14, pp. 6890–6900, 2009. [Online]. Available: https://doi.org/10.1021/ie900250g 93

[21] C. L. Yaws, *Thermophysical Properties os Chemicals and Hydrocarbons.* Lamar University Beaumont, Texas, Elsevier, 2009. 94