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On the Self-Consistency of Three-Parameter Corresponding-States Equations for Vapor Pressure

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ABSTRACT: Most of the three parameter corresponding-states equations proposed for estimating vapor pressures use the critical temperature T_c, the critical pressure P_c and Pitzer's acentric factor ω as input parameters. These equations must be self-consistent, i.e. they must reproduce the value of ω used as an input. In this work, we have checked this consistency for nine well-known vapor-pressure equations and we have found that it is satisfied with high accuracy for most of them, but not for all. On the basis of this consistency, we propose some conditions that can help to reduce the number of fitting coefficients in this type of vapor-pressure equations.

INTRODUCTION

The two-parameter corresponding-states principle (CSP) uses the temperature T_c and the pressure P_c of the critical point to characterize the thermodynamic behavior of a fluid. The CSP establishes that fluids at equal reduced conditions should behave identically. A paradigmatic expression in this framework is the Guggenheim equation for the temperature dependence of the vapor pressure along the liquid−vapor coexistence curve[1]

$$\ln P_r = 5.4\left(1-\frac{1}{T_r}\right) \tag{1}$$

where $P_r = P/P_c$ is the reduced saturation vapor pressure and $T_r = T/T_c$ is the reduced temperature. Guggenheim derived eq 1 on the basis of the Clausius−Clapeyron equation by fitting experimental data for a small number of simple, nonpolar fluids.

In order to extend the CSP to a wider range of fluids, including polar fluids, a third or even a fourth parameter has been introduced in the corresponding-states correlations. In particular, in the three-parameter CSP the most commonly used and most reliable third parameter is the Pitzer acentric factor ω defined by[2,3]

$$\omega = -1.0 - \log_{10} P_r \qquad \text{at} \quad T_r = 0.7. \tag{2}$$

Although the acentric factor was originally introduced to represent the acentricity or nonsphericity of a molecule, nowadays it is used as a measure of the complexity of a molecule with respect to its size/shape and polarity and it is tabulated for many substances.[4]

In general, in the Pitzer three-parameter corresponding-states theory, a vapor-pressure equation has the form

$$\ln P_r = f(T_r;\omega) \tag{3}$$

with $f(1;\omega) = 0$. Furthermore, taking into account definition 2, the function $f(T_r;\omega)$ must satisfy the condition

$$f(0.7;\omega) = -(1+\omega)\ln 10 \tag{4}$$

in order to be self-consistent. In this work, we check condition 4 for nine vapor-pressure equations of the form of eq 3 reported in the literature and widely used for estimating the vapor pressures of a great variety of fluids. Furthermore, as an instructive application, we shall use condition 4 to build a three-parameter corresponding-states vapor-pressure equation on the basis of the Clausius−Clapeyron equation that provides theoretical support to the Guggenheim equation.

CHECKING SELF-CONSISTENCY OF VAPOR-PRESSURE EQUATIONS

Most of the vapor-pressure equations of the form of eq 3 proposed in the literature are expressed as a power series of ω,

$$\ln P_r = f(T_r;\omega) = \sum_{k=0}^{n} \omega^k f_k(T_r) \tag{5}$$

where $f_k(1) = 0$. We note that the functions $f_k(T_r)$ usually have the same analytical form for different values of k but including different adjustable parameters. To our knowledge, only linear ($n = 1$) and quadratic ($n = 2$) equations have been proposed. Those used in the present work are reported in Table 1. Five of them are linear in ω [Lee−Kesler[5] (LK), Schreiber−Pitzer[6] (SP), Brandani[7] (B1), Twu−Coon−Cunningham[8] (TCC), and Mejbri−Bellagi[9] (MB)] and three are quadratic in ω [Ambrose−Walton[10] (AW), Brandani[7] (B2), and Xiang[11] (X)].

From eq 5, the self-consistency condition 4 leads to

$$\sum_{k=0}^{n} \omega^k f_k(0.7) = -(1+\omega)\ln 10 \tag{6}$$

and therefore, the temperature functions $f_k(T_r)$ must satisfy the following conditions

$$f_0(0.7) = -\ln 10, \quad f_1(0.7) = -\ln 10, \quad \text{and} \quad f_{k\geq 2}(0.7) = 0 \tag{7}$$

The values of $f_k(0.7)$ for the vapor pressure equations of Table 1 are reported in Table 2. According with eq 7, the values

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Table 1. Three-Parameter Corresponding-States Equations for Vapor Pressure Used in This Work[a]

equation	n	$f_k(T_r)$
LK[5]	1	$A_k + \frac{B_k}{T_r} + C_k \ln T_r + D_k T_r^{6}$
SP[6]	1	$\left[A_k + \frac{B_k}{T_r} + C_k \log_{10} T_r + D_k T_r\right] \ln 10$
B1[7]	1	$\frac{1}{T_r}[A_k(1-T_r) + B_k(1-T_r)^{1.5} + C_k(1-T_r)^{2.5} + D_k(1-T_r)^{5} + E_k(1-T_r)^{10}]$
TCC[8]	1	$\frac{1}{T_r}[A_k(1-T_r) + B_k(1-T_r)^{1.5} + C_k(1-T_r)^{3} + D_k(1-T_r)^{6}]$
MB[9]	1	$A_k\left[\frac{1}{T_r} - \exp\left(1-\frac{1}{T_r}\right)\right] + B_k\left[\left(\frac{1}{T_r}\right)^{C_k} - \exp\left(1-\frac{1}{T_r}\right)\right]$
AW[10]	2	$\frac{1}{T_r}[A_k(1-T_r) + B_k(1-T_r)^{1.5} + C_k(1-T_r)^{2.5} + D_k(1-T_r)^{5}]$
B2[7]	2	$\frac{1}{T_r}[A_k(1-T_r) + B_k(1-T_r)^{1.5} + C_k(1-T_r)^{2.5} + D_k(1-T_r)^{5} + E_k(1-T_r)^{10}]$
X[11]	2	$[A_k + B_k(1-T_r)^{1.89} + C_k(1-T_r)^{5.67}] \ln T_r$

[a] The equations have the form given by eq 5. The values of the coefficients can be found in the corresponding references.

of $f_0(0.7)$ and $f_1(0.7)$ must be compared with the value $-\ln 10 = -2.30258509...$, while $f_2(0.7)$ must be compared with zero. In parentheses we show the absolute percent deviations between $f_0(0.7)$ or $f_1(0.7)$ and $-\ln 10$. For linear equations in ω, we can see that such deviations are very small ($\approx 10^{-3}$ % or smaller) for the LK, SP, and TCC equations, indicating the high self-consistency of these equations to reobtain the acentric factor value used as an input. The B1 equation presents a good accuracy for $f_0(0.7)$ but not for $f_1(0.7)$. The MB equation presents a fairly good accuracy for both $f_0(0.7)$ and $f_1(0.7)$. In what respect to the quadratic equations in ω, we can see that while the AW and B2 equations are highly self-consistent in ω, the X equation deviates appreciably from the conditions of eq 7. It should be noted that Xiang proposed his equation as a four-parameter corresponding-states equation including the factor $\theta = (Z_c - 0.29)^2$, where Z_c is the critical compressibility factor, as a fourth parameter accounting for the main effects of highly nonspherical molecules. For nonpolar substances, θ can be approximated by $\theta = 0.0064\omega^2$ and X equation becomes a three-parameter corresponding-states equation quadratic in ω. This quadratic form for the Xiang equation is the one considered in the present work.

Other three-parameter corresponding-states equations for vapor pressure have the form

$$\ln P_r = f(T_r; \omega) = \sum_{k=1}^{n} A_k(\omega)\, g_k(T_r) \qquad (8)$$

where the functions $A_k(\omega)$ include several fitting parameters and the temperature functions $g_k(T_r)$ usually are simple functions without fitting parameters and they satisfy $g_k(1) = 0$. The application of the self-consistency condition 4 into eq 8 yields

$$\sum_{k=1}^{n} A_k(\omega)\, g_k(0.7) = -(1+\omega) \ln 10 \qquad (9)$$

The knowledge of the functions $A_k(\omega)$ is required in order to obtain conditions more detailed than that of eq 9. Nevertheless,

Table 2. Values for the Temperature Functions $f_k(0.7)$ of the Vapor-Pressure Equations Reported in Table [1,a]

equation	$f_0(0.7)$	$f_1(0.7)$	$f_2(0.7)$
LK	-2.30257517 (4.3×10^{-4} %)	-2.30248585 (4.3×10^{-3} %)	
SP	-2.30258515 (2.3×10^{-6} %)	-2.30258478 (1.3×10^{-5} %)	
B1	-2.30258477 (1.4×10^{-5} %)	-2.37275480 (3.05 %)	
TCC	-2.30258335 (7.6×10^{-5} %)	-2.30258400 (4.8×10^{-5} %)	
MB	-2.29978320 (0.12 %)	-2.31791667 (0.67 %)	
AW	-2.30258674 (7.2×10^{-5} %)	-2.30258533 (1.0×10^{-5} %)	6.33227×10^{-7}
B2	-2.30258477 (1.4×10^{-5} %)	-2.30258750 (1.6×10^{-4} %)	1.18145×10^{-6}
X	-2.25747541 (1.96 %)	-2.66086936 (15.56 %)	-3.34455×10^{-2}

[a] The absolute percent deviations for $f_0(0.7)$ and $f_1(0.7)$ respect to the value $-\ln 10$ are shown in parentheses.

since most fluids have values of ω comprised between 0 and 1, two possible conditions to check the self-consistency of eq 8 are

$$f(0.7, 0) = \sum_{k=1}^{n} A_k(0)\, g_k(0.7) = -\ln 10 \tag{10}$$

and

$$f(0.7, 1) = \sum_{k=1}^{n} A_k(1)\, g_k(0.7) = -2\ln 10 \tag{11}$$

The following equation of the form of eq 8 was proposed by Edelat et al.[12] for estimating the vapor pressure of hydrocarbons:

$$\ln P_r = \frac{1}{T_r}\left[A_1(\omega)\left(1-\frac{1}{T_r}\right) + A_2(\omega)\left(1-\frac{1}{T_r}\right)^{1.5} + A_3(\omega)\left(1-\frac{1}{T_r}\right)^{3} + A_4(\omega)\left(1-\frac{1}{T_r}\right)^{6}\right] \tag{12}$$

From the analytical expressions for the functions $A_k(\omega)$ reported by these authors[12] one has

$$f(0.7, 0) = -2.3025737 \quad \text{and} \quad f(0.7, 1) = -4.6051447 \tag{13}$$

which present absolute percent deviations of 4.9×10^{-4} % and 1.1×10^{-3} % with respect to the conditions given by eq 10 and eq 11. This shows that eq 12 presents a high degree of self-consistency in the acentric factor ω.

A SIMPLE APPLICATION

As a nice, instructive application of the self-consistency condition (4) we consider the construction of a three-parameter corresponding-states equation for vapor pressure on the basis of the Clausius−Clapeyron equation. Substituting $f_k = A_k(1 - 1/T_r)$ into the series expansion (5) one obtains

$$\ln P_r = \sum_{k=0}^{n} \omega^k A_k \left(1-\frac{1}{T_r}\right) \tag{14}$$

where, taking into account the conditions of eq 7 one has

$$A_0 = A_1 = \frac{7\ln 10}{3} \quad \text{and} \quad A_{k\geq 2} = 0 \tag{15}$$

and eq 14 becomes the well-known equation[13]

$$\ln P_r = \frac{7\ln 10}{3}(1+\omega)\left(1-\frac{1}{T_r}\right) \tag{16}$$

Since $(7/3)\ln 10 = 5.37... \approx 5.4$, eq 16 becomes 1 for $\omega = 0$; that is, the Guggenheim vapor-pressure equation is the zeroth order (spherical) contribution to the three-parameter corresponding-states form of the Clausius−Clapeyron equation. This supports the choice of the acentric point ($T_r = 0.7$) as an useful reference point in the vapor-pressure curve.

CONCLUSIONS

Most of the three-parameter corresponding-states equations proposed in the literature for estimating the vapor pressure of pure fluids use the temperature and pressure of the critical point and the acentric factor as input parameters. Such equations must show self-consistency to reobtain the same value for the acentric factor than the one used as an input. This self-consistency can be used for testing the existing vapor-pressure equations or for reducing the number of adjustable coefficients appearing in them. We have checked this acentric factor self-consistency for nine vapor pressure equations often used for estimating the vapor pressure of a great variety of fluids. We have found that most, but not all, of the analyzed equations present a high degree of self-consistency. This is an example showing that care should be taken in order to include coherent information in predicting or in correlating equations.

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