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INVESTIGATION AND IMPROVEMENT OF THE HORVÁTH-LIN EQUATION OF STATE

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SUMMARY

In connection with a thermodynamic analysis of high-performance liquid chromatography, Horváth and Lin developed a three-parameter equation of state. The dimensionless multipliers of this equation were correlated with the critical compressibility factor, z_c . A different temperature-correction relationship is now suggested. It is shown that the coefficient m in the modified temperature correction is component-specific and, with polar substances, it is also temperature dependent. Equations that correlate it with the acentric factor and with the polarity factor are given.

INTRODUCTION

Horváth and Lin¹ proposed the following three-parameter equation of state with a critical compressibility factor correlation:

$$P = RT/(v - b) - a/\gamma(v + c) \quad (1)$$

where

$$a = \alpha a[T_r](R^2 T_c^2/P_c) \quad (2)$$

with $a[T_r]$ given by eqn. 15;

$$b = \beta(RT_c/P_c) \quad (3)$$

$$c = \gamma b \quad (4)$$

The root of eqn. 1 at the critical temperature, T_c , and critical pressure, P_c , is the reference volume of the fluid, v_0 ; α , β and γ are dimensionless multipliers which are interrelated and dependent on the reference compressibility factor, z_0 :

$$z_0 = (P_c v_0)/(RT_c) \quad (5)$$

The dimensionless multipliers are involved in the following system of equations derived from the canonical form of the critical isotherm:

$$z_0^3 = \alpha\beta \quad (6)$$

$$3z_0^2 = -\gamma\beta^2 - \gamma\beta + \alpha \quad (7)$$

$$3z_0 = -\gamma\beta + \beta + 1 \quad (8)$$

The numerical solution of this non-linear system of equations is given as the following cubic polynomials of the reference compressibility factor, z_0 :

$$\alpha = 0.12233 + 5.22425z_0 - 22.4011z_0^2 + 28.43065z_0^3 \quad (9)$$

$$\beta = 1.494495 - 14.62351z_0 + 47.4259z_0^2 - 48.69008z_0^3 \quad (10)$$

$$\gamma = 1657.483 - 16001.19z_0 + 51711.96z_0^2 - 55874.32z_0^3 \quad (11)$$

$$b_r - b_r^0 = 3.287697 - 35.07038z_0 + 116.9788z_0^2 - 124.1009z_0^3 \quad (12)$$

where b_r is the reduced limiting volume ($b_r = b/v_0$).

The Horváth–Lin equation of state is one of the possible realizations of the three-parameter corresponding states principle:

$$f[P, v, T; P_c, T_c, z_c] = 0 \quad (13)$$

with the critical compressibility factor, z_c , selected as the third parameter. The correlation between the critical compressibility factor, z_c , and the reference compressibility factor, z_0 , is calculated from the data in the original Horváth–Lin paper and is

$$z_0 = -0.4734192 + 7.320713z_c - 23.58415z_c^2 + 27.45711z_c^3 \quad (14)$$

It is obvious that eqn. 14 and the relationships expressed in eqns. 9–12 generate a family of Horváth–Lin equations of state (eqn. 1) with critical compressibility factor correlation. For example, if we take the premultiplier γ as equal to unity, then $b = b_r^0$ and eqn. 1 simplifies to the Redlich–Kwong equation of state². It can be seen that the presence of the third parameter, c , in the Horváth–Lin equation of state is responsible for the value of the component-specific reduced limiting volume, $b_r = b/v_0$, and consequently for the profile of the isotherm. Because of this, the calculated isotherm fits the experimental P – v curve.

In the original Horváth–Lin paper, the dimensionless coefficient $a[T_c]$ is suggested to be given by

$$a[T_c] = 1/T_r \quad (15)$$

Our investigations proved that this relationship limits the performance of eqn. 1.

IMPROVEMENT OF THE HORVÁTH-LIN EQUATION OF STATE FOR APOLAR SUBSTANCES

The coefficient $a[T_r]$ is certainly component-specific and its temperature dependence is slightly more complicated than suggested by eqn. 15. We selected another relationship, which was first proposed by Soave³:

$$a[T_r] = [1 + m(1 - T_r^{0.5})]^2 \quad (16)$$

Here the component-specific parameter $m = m_s$ is correlated with Pitzer's acentric factor⁴, ω :

$$m_s = 0.48036 + 1.5701\omega - 0.16814\omega^2 \quad (17)$$

Pitzer's acentric factor is very component-specific:

$$\omega = -\log P_r^0 - 1 \quad (T_r = 0.7) \quad (18)$$

However, in the case of the Horváth-Lin equation of state, not only α , β , γ and b_r are functions of z_o , but also the parameter from eqn. 16. We have found that the following two-variable polynomial shows this phenomenon:

$$\begin{aligned} m_{o,7} = & (0.48036 + 1.5701\omega - 0.16814\omega^2) + \\ & + (0.57200 + 0.48044\omega - 0.08144\omega^2)(b_r - b_r^0) + \\ & + (-5.0607 - 4.2736\omega + 0.80413\omega^2)(b_r - b_r^0)^2 \end{aligned} \quad (19)$$

Applying eqn. 1 together with eqn. 16 and with the correction expressed in eqn. 19 represents the first improvement of the Horváth-Lin equation of state. In the class of apolar substances there is a correlation between ω and z_c :

$$z_c = 0.291 - 0.08\omega \quad (20)$$

Taking into account this relationship, we can consider that the acentric factor, ω , and the critical compressibility factor, z_c , carry the same information about the shape and size of a molecule. Thus, with this first improvement of the Horváth-Lin equation of state suggested here for apolar substances we do not leave the domain of the three-parameter corresponding states principle.

Improvement of the Horváth-Lin equation of state for polar substances

The correlation expressed in eqn. 20 loses its validity with polar substances. It is true that the critical compressibility factor, z_c , and the acentric factor, ω , carry different information about the size and shape of a molecule on the one hand, and about its polarity on the other. There is a departure from the relationship expressed in eqn. 20, however, and its interpretation would be very difficult. Consequently, we have to apply the four-parameter corresponding states principle for polar substances.

We selected the polarity factor as the fourth parameter, by a definition similar to eqn. 16:

$$\omega_p = -\log P_r^0 - 1 \quad (T_r = 0.6) \quad (21)$$

This definition corresponds to the fact that the lower the temperature, the better will the polarity of the molecule manifest itself. Hence the difference in the acentric factor, ω , and the polarity factor is very significant. We have found a two-variable polynomial for the component-specific parameter $m_{0.6}$:

$$\begin{aligned} m_{0.6} = & (-0.07725 + 1.0699\omega_p - 0.1252\omega_p^2 + 0.013377\omega_p^3) + \\ & + (-0.36434 + 0.3236\omega_p - 0.6249\omega_p^2 + 0.009049\omega_p^3)(b_r - b_r^0) + \\ & + (-3.2220 - 2.8792\omega_p - 0.5501\omega_p^2 + 0.0791225\omega_p^3)(b_r - b_r^0)^2 \quad (22) \end{aligned}$$

The value of m in eqn. 16 at the reduced temperature of $T_r = 0.7$ has to be $m = m_{0.7}$, and at the reduced temperature of $T_r = 0.6$ it has to be $m = m_{0.6}$. This means that m is a temperature-dependent coefficient in eqn. 16. One can calculate m for temperatures $T_r > 0.34$ by the following linear relationship:

$$m = (10T_r - 6)(m_{0.7} - m_{0.6}) + m_{0.6} \quad (23)$$

Applying eqn. 1 with eqn. 16 and together with the correlations expressed in eqns. 10 and 22 involved in the relationship expressed in eqn. 23 represents, for polar substances, the second improvement of the Horváth–Lin equation of state.

HOW TO USE THE IMPROVED HORVÁTH–LIN EQUATION OF STATE

Let us consider eqn. 1 in a detailed form:

$$\begin{aligned} [RT/(v - \beta[z_0](RT_c/P_c)) - \{\alpha[z_0](R^2T_c^2/P_c)\{1 + m[\omega, \omega_p, (b_r - b_r^0)[z_0]]\}(1 - T_r^{0.5})^2\}]/ \\ v\{v - \gamma[z_0]\beta[z_0](RT_c/P_c)\} - P[v, T] = 0 \quad (24) \end{aligned}$$

This is a non-linear equation with only one unknown variable, z_0 . Fitting eqn. 24 to a single experimental point $[P, v, T]$, one can calculate the value of the unknown variable, z_0 . Knowing z_0 , ω and ω_p for the given substance, one can use the improved Horváth–Lin equation of state for direct calculation.

The correlations between z_c and z_0 for polar and apolar substances would eliminate the determination of z_0 by the mentioned fitting procedure. Elaboration of such correlations will be the subject of another paper.

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