**An Analytical Method of Predicting Lee-Kesler-Plöcker
Binary Interaction Coefficients –
Part I: For Non-Polar Hydrocarbon Mixtures**

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ABSTRACT

An analytical method is proposed for finding numerical values of binary interaction coefficients for non-polar hydrocarbon mixtures when the Lee-Kesler (LK) equation of state is applied. The method is based on solving simultaneous equations, which are Plöcker's mixing rules for pseudocritical parameters of a mixture, and the Lee-Kesler equation for the saturation line.

For a hydrocarbon mixture, the method allows prediction of κ_{ij} interaction coefficients (ICs) which are close to values obtained by processing experimental p-v-t data on the saturation line and subsequent averaging. For mixtures of hydrocarbon molecules containing from 2 to 9 carbon atoms, the divergence between calculated and experimentally based ICs is no more than $\pm 0.4\%$.

The possibility of extending application of this method to other non-polar substances is discussed.

KEYWORDS: algorithm; binary interaction coefficient; calculation; equation of state; mixture; non-polar substance; thermophysical properties.

1. INTRODUCTION

In 1975 Lee and Kesler proposed an equation of state for pure non-polar substances and described mixing rules for calculating pressure-volume-temperature (p-v-t) and thermodynamic properties of mixtures, but binary interaction coefficients were not mentioned in this original work.¹ In order to calculate the pseudocritical temperature of mixtures, the authors proposed the well known equation:

$$T_{cmix} = (1/V_{cmix}) \sum_{ij} \chi_i \chi_j V_{cij} T_{cij} , \quad (1)$$

where: T_{cmix} is the pseudocritical temperature of a mixture, K;

$V_{cmix} = \sum_{ij} \chi_i \chi_j V_{cij}$, is the pseudocritical molar volume of a mixture, cm^3/gmol ;

$$V_{cij} = (1/8) (V_{ci}^{1/3} + V_{cj}^{1/3})^3 ;$$

$$T_{cij} = (T_{ci} \cdot T_{cj})^{1/2} \cdot \kappa_{ij} ;$$

V_{ci} , V_{cj} are critical molar volumes of the components i and j correspondingly, cm^3/gmol ;

T_{ci} , T_{cj} are critical temperatures of the components i and j correspondingly, K; χ_i , χ_j

are molar fractions of the components i and j correspondingly; κ_{ij} equals one.

In 1978 V. J. Plöcker, H. Knapp, and J. Prausnitz extended this work by publishing work applying the Lee and Kesler equation of state to phase equilibrium analysis in mixtures of non-polar substances with a considerable difference in critical

parameters.² For this purpose the authors established that equation (1) did not agree with the experimental data, and they offered another formula for the pseudocritical temperature of a mixture:

$$T'_{cmix} = \left(\frac{1}{V^{\eta}_{cmix}} \right) \sum_{ij} x_i x_j V^{\eta}_{cij} T'_{cij} \quad (2)$$

where: $T'_{cij} = (T_{ci} \cdot T_{cj})^{1/2} \cdot \kappa_{ij0.25}$

η is an empirical coefficient and $\kappa_{ij0.25}$ is a binary interaction coefficient (IC) that does not depend on composition, pressure and temperature. The authors assigned a universal numerical value of 0.25 to η , which they obtained by processing experimental data. The $\kappa_{ij0.25}$ was considered to be a fitting parameter determined by processing experimental data exclusively. Numerical values of $\kappa_{ij0.25}$ were calculated by the authors for approximately one hundred binary combinations of non-polar components, and an empirical correlation of these κ_{ij} 's for mixtures of hydrocarbons and other non-polar molecules was established as a function of the parameter $(V_{ci} T_{ci})/(V_{cj} T_{cj})$. Henceforth, whenever the Lee and Kesler (LK) equation of state was used for mixture analysis, the mixing rule indicated by equation (2) and κ_{ij} 's determined by processing available experimental data were used for the thermodynamic property calculations.

In this manner the main advantage of the LK equation, which is the ability to calculate properties of mixtures by making use of critical parameters of pure components, was compromised. The original LK equation provided the opportunity

parameters might be estimated by a group contribution method from only a structural formula. Several unsuccessful attempts were made to restore this advantage by predicting $\kappa_{ij0.25}$ from component parameters.³ This lack of success is not surprising, because $\kappa_{ij0.25}$ is a unique fitting parameter that depends not only on properties of components but also on the extent to which the LK equation (and the models of Benedict-Webb-Rubin (BWR) and Pitzer relation that are built-in) correspond to the physical nature of substances and their mixtures.^{4,5} It is necessary to remember that the basic BWR equation was developed for natural gas property analysis, and the Pitzer relation is good only for non-polar substances like hydrocarbons. Meanwhile, the LK equation has come to be broadly used for various substances and their mixtures including polar substances.

Additionally, the optimal values of $\kappa_{ij0.25}$ differ for different thermophysical properties, and various authors optimize $\kappa_{ij0.25}$ by means of different minimization functions working with different properties.⁶ As a result, the set of $\kappa_{ij0.25}$ values reported in the literature is badly generalized and shows a large range of variability. It is understandable that $\kappa_{ij0.25}$ values obtained by different authors for the same mixture differ considerably (Table I).⁶ So, for non-polar and polar mixtures, the development of an analytical method intended for predicting κ_{ij} values only on the basis of mixture component parameters is still a very compelling problem. In Part I of this article, the problem is solved for mixtures of non-polar substances.

2. INTERACTION COEFFICIENT CALCULATION

In this work an attempt is made to predict the $\kappa_{ij0.25}$ values analytically, to develop a fundamentally grounded method for the $\kappa_{ij0.25}$ value prediction, and to estimate the importance of factors that impact the accuracy of the prediction. The most simple assumption that makes it possible to obtain the $\kappa_{ij0.25}$ value is:

$$T_{cmix} = T'_{cmix} \quad (3)$$

From this expression we have to find different values of $\kappa_{ij0.25}$ for each value of molar concentration, χ , and then to average them. Table II presents the $\kappa_{ij0.25exp}$ values from reference 2 and the $\kappa_{ij0.25calc}$ values found from equation (3); the formula used for averaging is:

$$\kappa_{ij0.25calc} = \left(\sum_{\chi=0.1}^{0.9} \kappa_{ij} + 2 \right) / 11 ; \quad (4)$$

κ_{ij} values were determined over a range of molar compositions from 0.1 to 0.9 in 0.1 increments; the sum of values obtained was increased by two because $\kappa_{ij0.25} = 1$ when $\chi = 0$, and $\chi = 1.0$. Table II shows that the calculated values track the experimental values well, but, naturally, differ from them, because formula (1) is not sufficiently accurate when mixtures of substances with large differences in critical parameters is encountered. It is evident that the multiplier, κ_{ij} , needed for T_{cij} in equation (1) differs more from 1.0 with greater differences in critical parameters of mixture components. The equations given in reference 1 were used to find the value of the multiplier.

Mixing rules of the pseudocritical parameters for a binary mixture assume the form:

$$T_{cmix} = \frac{\chi_1^2 V_{c1} T_{c1} + \chi_2^2 V_{c2} T_{c2} + 0.25 \chi_1 \chi_2 (V_{c1}^{1/3} + V_{c2}^{1/3})^3 \sqrt{T_{c1} T_{c2}} \cdot \kappa_{H1.0}}{\chi_1^2 V_{c1} + \chi_2^2 V_{c2} + 0.25 \chi_1 \chi_2 (V_{c1}^{1/3} + V_{c2}^{1/3})^3}, \quad (5)$$

$$V_{cmix} = \chi_1^2 V_{c1} + \chi_2^2 V_{c2} + 0.25 \chi_1 \chi_2 (V_{c1}^{1/3} + V_{c2}^{1/3})^3, \quad (6)$$

$$\omega_{mix} = \chi_1 \omega_1 + \chi_2 \omega_2, \quad (7)$$

$$Z_{cmix} = 0.2905 - 0.085 \omega_{mix}, \quad (8)$$

$$\omega = \frac{\ln P_{br}^s - 5.92714 + 6.09648/T_{br} + 1.28862 \ln T_{br} - 0.169347 T_{br}^6}{15.2518 - 15.6875/T_{br} - 13.4721 \ln T_{br} + 0.43577 T_{br}^6}, \quad (9)$$

where:

- $P_{br}^s = 1 \text{ atm}/P_c$
- $P_c = \text{critical pressure, atm}$
- $T_{br} = T_b/T_c$
- $T_b = \text{the saturated temperature under 1 atm, K.}$
- $\omega = \text{the acentric factor}$
- $Z_{cmix} = \text{the pseudocritical compressibility factor of the mixture}$
- $\kappa_{H1.0} = \kappa_H \text{ if } \eta = 1.0$

Then, knowing that $\ln P_{br}^s = \ln(1) - \ln P_c = -\ln P_c$ and using the following functions:

$$A = 15.2518 - 15.6875/T_{br} - 13.4721 \ln(T_{br}) + 0.43577 T_{br}^6,$$

$$B = -5.92714 + 6.09648/T_{br} + 1.28862 \ln(T_{br}) - 0.169347 T_{br}^6$$

and using equations (7) and (9) equation (10) can be derived.

$$P_{cmix} = \frac{P_{c1}^{x_1 A_{mix}/A_1} \cdot P_{c2}^{x_2 A_{mix}/A_2}}{e^{x_1 B_1 A_{mix}/A_1 + x_2 B_2 A_{mix}/A_2 - B_{mix}}}, \quad (10)$$

where:

$$\begin{aligned} P_{cmix} &= \text{the pseudocritical pressure of a mixture, atm.} \\ A_{mix} &= f_1[(T_v/T_c)_{mix}] \text{ for a mixture} \\ B_{mix} &= f_2[(T_v/T_c)_{mix}] \text{ for a mixture} \\ A_1 &= f_1[(T_v/T_c)_1] \text{ for a component 1} \\ A_2 &= f_1[(T_v/T_c)_2] \text{ for a component 2} \\ B_1 &= f_2[(T_v/T_c)_1] \text{ for a component 1} \\ B_2 &= f_2[(T_v/T_c)_2] \text{ for a component 2} \end{aligned}$$

$(T_v/T_c)_{mix}$ is the pseudoparameter of a mixture, and the functions of f_1 and f_2 are those shown for A and B above. Equation (10) fits the hypothesis that the LK equation is based on: that a mixture is a pseudosubstance. Using equation (10) the following may be determined:

$$T_{cmix} = \frac{P_{cmix} V_{cmix}}{RZ_{cmix}} \quad (11)$$

where: $R = 82.04$, (gas law constant; $[\text{atm-cm}^3]/[\text{mole-}^\circ\text{K}]$).

If equation (11) is set equal to equation (5), an equation with two unknowns, $(T_v/T_c)_{mix}$ and $\kappa_{ij1.0}$, results. The dependence of $(T_v/T_c)_{mix}$ on χ is defined by the change of two parameters: T_{cmix} and T_{bmix} both are pseudoparameters. The dependence of T_{cmix} on molar composition is given by equation (5); an equation similar to equation (5) can be written for the pseudoparameter T_{bmix} :

$$T_{\text{bmix}} = \frac{x_1^2 V_{c1} T_{b1} + x_2^2 V_{c2} T_{b2} + 0.25 x_1 x_2 (V_{c1}^{1/3} + V_{c2}^{1/3})^3 \sqrt{T_{b1} T_{b2}} \kappa_{12}}{x_1^2 V_{c1} + x_2^2 V_{c2} + 0.25 x_1 x_2 (V_{c1}^{1/3} + V_{c2}^{1/3})^3}, \quad (12)$$

where: $\kappa_{ij0} = 1/\kappa_{ij1.0}$; T_{b1} , T_{b2} are normal boiling temperatures of the components 1 and 2. Setting equation (11) equal to equation (5) and implementing equation (12), will result in an equation with only one unknown $\kappa_{ij1.0}$. With these $\kappa_{ij1.0}$ values, the $\kappa_{ij0.25}$ values may be calculated by setting equation (11) equal to equation (2) for each value of χ and subsequent averaging in accordance with equation (4).

3. RESULTS

In Figure 1, the $\kappa_{ij0.25\text{exp}}$ values are presented, which have been obtained by processing experimental data for mixtures of hydrocarbons containing components with 2-9 carbon atoms in their structure, and the $\kappa_{ij0.25\text{calc}}$ values obtained by the method described above.² When the $\kappa_{ij0.25\text{calc}}$ values were obtained, equation (8) was used to determine Z_{cmix} . For some mixtures, the experimental data show values that slightly differ from calculated values. This can be explained with the help of Figure 2. This figure shows that the actual Z_c values of components (and, consequently, Z_{cmix}) are sometimes different from the values obtained from equation (8).

The maximum divergence between the calculated and experimental κ_{ij} values (that is % $\kappa_{ij\text{calc}}$) was approximately $\pm 0.4\%$ with an average divergence $\pm 0.1\%$, which may be considered quite satisfactory (see Figure 1).

In Figure 3. the change of the calculated $(T_v/T_c)_{\text{mix}}$ values is plotted against the pseudocritical volume of the mixture, V_{cmix} for ethane-propane and ethane-nonane mixtures. The change of the (T_v/T_c) value against V_c for pure hydrocarbons $C_1 - C_9$ is also shown. The functions almost coincide which confirms the validity of the hypothesis describing a mixture as a pseudosubstance.

4. CONCLUSIONS

The method outlined above makes it possible to obtain binary interaction coefficients values, κ_{ij} , for the LK equations of state with an average deviation of 0.1% using the critical parameters of mixture components, and their normal boiling temperatures, T_b . The method does not have any restrictions imposed by the nature of the components and may be recommended as a general method for calculating the κ_{ij} values when the LK equation of state is applied to mixtures of non-polar substances.

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Table I. Variations in Lee-Kesler-Plöcker Interaction Coefficient from Experimental Data

Mixture	Author	$\kappa_{ij} (x,y)$	$\kappa_{ij} (V_L)$	$\kappa_{ij} (C_p)$
R-22/R-114	Hackstein	0.963	----	----
	Kruse	0.975	0.975	----
	Ström	0.979	1.042	----
	Valtz	0.973	0.973	----
	Radermacher	----	----	0.97
R-22/R-142b	Lavue	0.993	0.997	----
	Ström	1.005	1.096	----
	Valtz	1.00	1.046	----
	Kruse	----	1.038	----
	Radermacher	----	----	1.04
R-22/R-152a	Lavue	1.013		----
	Ström	1.014		----
	Kruse	----		----
	Radermacher	----		1.02

Table II. Comparison of Experimental to Calculated Lee-Kesler-Plöcker Interaction Coefficients Using Equation (3)

κ_{ij}	Mixture						
	ethane & propane	ethane & n-butane	ethane & n-pentane	ethane & n-hexane	ethane & n-heptane	ethane & n-octane	ethane & n-nonane
	C_2, C_3	C_2, C_4	C_2, C_5	C_2, C_6	C_2, C_7	C_2, C_8	C_2, C_9
$\kappa_{ijexp.}$	1.01	1.029	1.064	1.106	1.143	1.165	1.214
$\kappa_{ijcalc.}$	1.0113	1.0333	1.0605	1.0873	1.1147	1.1417	1.1676

FIGURE CAPTIONS (Part I)

Figure 1. Comparison of experimental to calculated interaction coefficients for mixtures of ethane with longer, straight-chain alkanes through n-nonane, and relative deviation of experimental versus calculated κ_{ij} 's: $\square$ — $\kappa_{ij0.25\text{ exp}}$; $+$ — $\kappa_{ij0.25\text{ calc}}$; $\diamond$ — $\% \kappa_{ij}$ deviation.

Figure 2. Experimental and calculated compressibility factors, Z_ω , obtained from equation (8), plotted against the acentric factor, ω , for methane (1) through n-decane (10): $\diamond$ — experimental; — — — — calculated.

Figure 3. The reduced boiling temperature, T_b/T_c , of pure substances C_1 — C_9 , and the reduced pseudo-boiling temperature, $(T_b/T_c)_{\text{mix}}$, for mixtures of ethane/nonane and ethane/propane plotted against critical volumes (V_c , $V_{c,\text{mix}}$): $+$ — $(T_b/T_c)_{\text{mix}}$ for ethane/nonane; $\diamond$ — $(T_b/T_c)_{\text{mix}}$ for ethane/propane; $\bullet$ — T_b/T_c for C_1 — C_9 .