Prediction of Vapor-Liquid Equilibria of Petroleum Fractions

PAUL G. MIKOLAJ and LACHHMAN DEV

University of California, Santa Barbara, California

The thermodynamic treatment of phase equilibria proposed by Chueh and Prausnitz has been modified to extend their method to systems of petroleum fractions. These modifications, which include the use of a symmetric convention for normalizing activity coefficients and replacement of the dilated van Laar model with a regular solution model, were required because existing data were insufficient to establish the needed binary interaction parameters. The resulting correlation was compared with experimental data on a naphtha-furnace oil mixture at conditions up to 660°F. and 517 lb./sq.in.abs. The computed *K* values showed an average absolute deviation of 9.1%, while *K* values predicted by the Chao-Seader correlation deviated by 12.4%.

A desirable feature of any correlation for predicting vapor-liquid equilibria is that it can be applicable to a wide variety of chemical species over a broad range of temperatures and pressures. For companies engaged in petroleum and petrochemical process design, this feature is not only desirable but also essential.

In a typical industrial organization, many computer programs are likely to be available for performing flash calculations or computing *K* values. Many of these programs may be optimum for a particular class of components or range of operating conditions. In addition, there will usually be one program of a utilitarian nature that can handle almost any system under practically all conditions and, consequently, will be the program that is most often employed. When the average design engineer, who is not an expert in solution thermodynamics, is faced with a choice of methods, he will more than likely select the tried and tested company standard rather than take a chance on a specialized correlation he is not familiar with. There is considerable incentive, therefore, to develop general usage correlations that are as accurate and reliable as possible.

It is an accepted fact that the Chao-Seader method (*1*) is currently the most widely used correlation in the area of petroleum and petrochemical design. The reasons for this wide acceptance are its generality and reasonable overall accuracy. One of the factors contributing to its generality is the availability of input data for a large number of components that are commonly encountered in the process industry. Moreover, even for components not considered as standard, the necessary input parameters can readily be estimated. Included in this latter category are those hydrocarbons classed as complex mixtures, that is, petroleum fractions. Thus the Chao-Seader correlation can handle with equal facility systems of known composition, systems of petroleum fractions, or combinations thereof.

Just as the Chao-Seader method was a significant improvement over previous techniques, there is much speculation that the recent work of Chueh and Prausnitz (*2*, *11*) will lead to still further improvement. This improvement, however, comes at the expense of increased input data requirements, particularly in the form of binary interaction parameters. Chueh and Prausnitz present parameters for a few systems in a series of recently published articles (*2* to *4*, *11*), and parameters for other systems can be obtained by reworking previously published experimental data. However, it is unlikely that sufficient experimental data exist to establish all the necessary parameters for the many systems of industrial or commercial interest. Therefore, while this new method is undoubtedly capable of greater predictive accuracy than the Chao-Seader method, its lack of immediate generality is likely to hamper or even prevent its adoption by industrial users.

The purpose of this paper is to explore means of extending the Chueh-Prausnitz correlation (hereafter referred to as the C-P correlation) to a class of components not covered in the original treatment, namely, systems of petroleum fractions. As explained in more detail later, this extension will necessitate that certain changes or modifications be made in the original treatment If, however, this modified treatment can predict *K* values for petroleum fractions with an accuracy comparable to the Chao-Seader method, industrial users may be less hesitant in adopting the C-P correlation for general use. By so doing, they can achieve improved accuracy for those systems whose input parameters are available and, at the same time, maintain current levels of accuracy for systems of petroleum fractions.

In the following sections of this paper, we briefly describe the C-P correlation and indicate the modifications necessary to extend it to systems of petroleum fractions. A comparison is then made between *K* values predicted by the modified treatment and those obtained experimentally for a petroleum fraction boiling from 86° to 750°F. A comparison is also made with the Chao-Seader correlation.

THE CHUEH-PRAUSNITZ CORRELATION

In their original treatment, Chueh and Prausnitz compute the *K* value for component *i* of a multicomponent system by the following equation:

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i^{(P^r)} f_i^{0(P^r)} \exp\left[(\bar{v}_i^L/RT)(P - P^r)\right]}{P\varphi_i} \qquad (1)$$

In this equation γ_i is the liquid-phase activity coefficient, f_i^0 is the standard state fugacity, φ_i is the vapor-phase fugacity coefficient, and $\bar{v}_i^L$ is the partial molar volume of component i in the liquid mixture. T is the temperature, P is the total pressure of the system, and the superscript P^r indicates that the property is computed at a specified reference pressure.

Despite the apparent simplicity of this equation, the evaluation of each term requires a considerable amount of

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Lachhman Dev is at Oregon State University, Corvallis, Oregon.

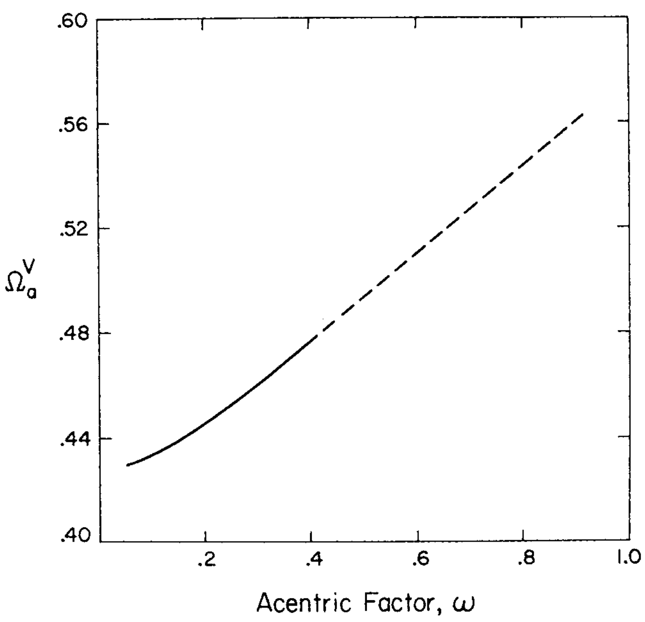

Fig. 1. Extrapolation of the dimensionless constant $\Omega_a{}^V$ in the Redlich-Kwong equation of state for saturated vapors.

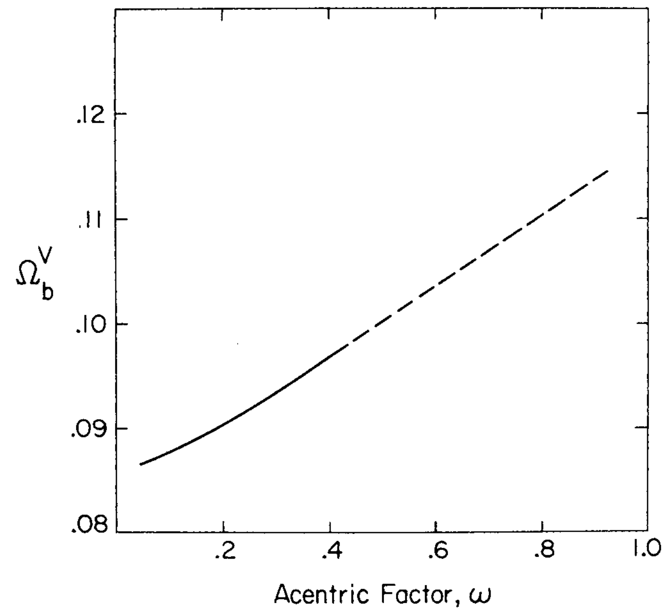

Fig. 2. Extrapolation of the dimensionless constant $\Omega_b{}^V$ in the Redlich-Kwong equation of state for saturated vapors.

data and computation. Since the data requirements are a central issue in the present work, they will be briefly discussed. The reader is referred to the original papers for a more detailed description.

The vapor-phase fugacity coefficient φ_i is evaluated by a modified Redlich-Kwong equation of state:

$$P = \frac{RT}{v - b} - \frac{a}{\sqrt{T}\, v(v + b)} \tag{2}$$

where

$$a = \Omega_a{}^V\, R^2\, T_c{}^{2.5}/P_c \tag{3}$$

$$b = \Omega_b{}^V\, R\, T_c/P_c \tag{4}$$

Whereas the original Redlich-Kwong equation (*12*) used universal values for $\Omega_a{}^V$ and $\Omega_b{}^V$ and required only pure component critical temperatures and pressures for the determination of φ_i, the modified equation requires the following additional parameters: the critical volume of each component, the acentric factor of each component, values of $\Omega_a{}^V$ and $\Omega_b{}^V$ for each component, and a constant characteristic of the *i-j* interaction for each binary pair in the system. While the first two of these additional requirements present no special problems, the last two are more difficult to obtain.

The same form of this equation is also used to compute the partial molar volume of components in the liquid phase. The data requirements are the same as for the vapor phase except that a different pair of dimensionless constants $\Omega_a{}^L$ and $\Omega_b{}^L$ must be specified for each component.

In order to avoid ambiguity when dealing with noncondensable or supercritical components, Chueh and Prausnitz elected to use the unsymmetric convention for normalizing liquid-phase activity coefficients. Thus, for those components whose critical temperature is near or below the temperature of the solution, the standard state fugacity is defined in terms of a Henry's constant. For subcritical components, the standard state fugacity is essentially the fugacity of the pure liquid. This approach therefore requires that Henry's constant be known for all solute-solvent pairs which exist at the solution temperature. And finally, liquid-phase activity coefficients are computed by means of a two-parameter dilated van Laar model. The data requirements for this model take the form of self-interaction constants for each binary pair and, depending on the solution temperature, dilation constants for the supercritical components.

In summary, then, application of the C-P method for the prediction of K values requires knowledge of four types of binary data: a characteristic constant for each *i-j* interaction, Henry's constants, self-interaction constants, and dilation constants. Also required, in addition to the usual pure component data, are two pairs of constants for use in the Redlich-Kwong equation of state.

DEVELOPMENT OF A MODIFIED CORRELATION

Although the original C-P treatment offers the possibility of a significant improvement in the accuracy of predicted K values, many of the required input parameters are not available in the literature. These data are scarce even for simple hydrocarbon systems and are totally nonexistent for systems of petroleum fractions. Therefore two avenues are open for extending the correlation to this latter type of system:

1. Develop estimation methods for determining the necessary parameters.
2. For those parameters that cannot be reliably estimated, modify the correlation by substituting a different method of computation.

In the following paragraphs, each term in the C-P correlation is examined relative to these two alternatives.

In discussing phase equilibria of petroleum fractions, we follow the customary treatment of dividing the true boiling point (TBP) distillation curve of the whole fraction into an arbitrary number of narrow boiling cuts or pseudocomponents. Each pseudocomponent is characterized by an average boiling point, specific gravity, and any other physical parameter that might be appropriate or available. The complex petroleum fraction can then be treated as a standard multicomponent system. The problem is thus reduced to one of determining the necessary properties of the N pure pseudocomponents and the $N(N - 1)/2$ pseudocomponent pairs.

Vapor-Phase Fugacity Coefficient

In order to evaluate the fugacity coefficient φ_i, the dimensionless constants in the Redlich-Kwong equation Ω_a^V and Ω_b^V must be estimated for each pseudocomponent. Values of these constants have been reported for 19 pure substances (*3, 11*) and show a relatively smooth trend when plotted against the acentric factor ω, as shown in Figures 1 and 2. These curves therefore have been extrapolated (as shown by the dotted lines) from the highest literature value ($\omega = 0.398$ for n-octane) to an acentric factor of about 0.9. Since the acentric factor of narrow boiling petroleum fractions can be estimated with a fair degree of reliability (*5*), these curves can be used to establish the appropriate values of Ω_a^V and Ω_b^V.

The other parameter needed for computing the vapor-phase fugacity is k_{ij}. This parameter is a binary constant characteristic of the i-j interaction and represents a deviation from the geometric mean for $T_{c_{ij}}$.

$$T_{c_{ij}} = (1 - k_{ij}) \sqrt{T_{c_{ii}}\, T_{c_{jj}}} \tag{5}$$

In general, k_{ij} must be obtained from some experimental information about the binary interaction, for example, second virial cross coefficients. For paraffin-paraffin systems, experimentally determined values of k_{ij} are reported to be in good agreement (*4, 11*) with the semitheoretical relation

$$k_{ij} = 1 - \left[\frac{\sqrt{v_{c_i}^{1/3} v_{c_j}^{1/3}}}{0.5\,(v_{c_i}^{1/3} + v_{c_j}^{1/3})} \right]^n \tag{6}$$

with $n = 3$. However, this equation is useful only for mixtures of paraffins and must be generalized before it can be applied to petroleum fractions of an arbitrary nature.

Since the UOP characterization factor U has long been used as a measure of paraffinicity (*5*), it was selected as a modifying parameter to account for deviations from paraffin-paraffin behavior. The following empirically determined expression for the exponent n in Equation (6) was found to give satisfactory results:

$$n = 3 \left(\frac{U_i/U_{p_i}}{U_j/U_{p_j}} \right)^{1.8} \tag{7}$$

$$U_i > U_j$$

In this equation, U_i is the characterization factor of pseudocomponent i and U_{p_i} is the characterization factor of a paraffin having the same boiling point as pseudocomponent i. The designation of i and j depends on the binary system under consideration.

A comparison of k_{ij} estimated from Equations (6) and (7) with literature values (*3, 11*) is given in Table 1. The petroleum fractions listed in this table are those used in testing the modified correlation and are described more completely in a following section.

Since all of the necessary input parameters are obtainable by estimation procedures, the vapor-phase fugacity coefficient for petroleum fractions can be computed in exactly the same manner as the original C-P correlation.

Liquid-Phase Partial Molar Volume

As described previously, the calculation of liquid-phase partial molar volumes requires a pair of dimensionless constants Ω_a^L and Ω_b^L in the Redlich-Kwong equation. As in the case of the vapor phase, these constants are given in the literature (*4, 11*) for several pure substances and also show a trend with respect to acentric factor. As shown in Figure 3, a plot of Ω_b^L versus ω is approximately linear and extrapolation beyond the final point ($\omega = 0.447$ for n-nonane) is straightforward. This straight line relationship, however, does not hold true in a similar plot of

TABLE 1. CHARACTERISTIC CONSTANT FOR i-j INTERACTION

Binary system	Computed k_{ij}*	Literature k_{ij}†
Methane:naphthalene	0.15	0.14
Methane:toluene	0.08	0.08
Ethane:cyclohexane	0.03	0.03
Propane:benzene	0.01	0.02
n-Octane-benzene	0.02	0.01
PF (135° to 156°):PF (400° to 450°)	0.02	——
PF (86° to 95°):PF (700° to 750°)	0.08	——

* Equations (6) and (7).
† References *3* and *11*.

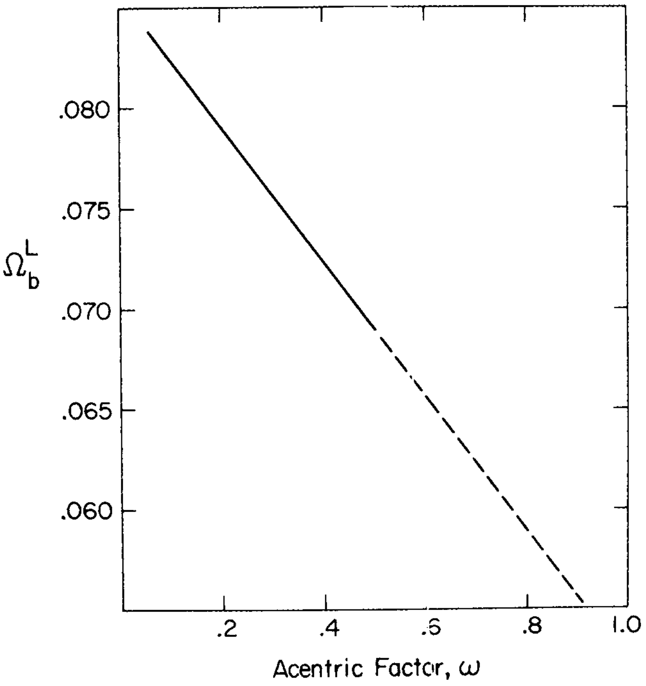

Fig. 3. Extrapolation of the dimensionless constant Ω_b^L in the Redlich-Kwong equation of state for saturated liquids.

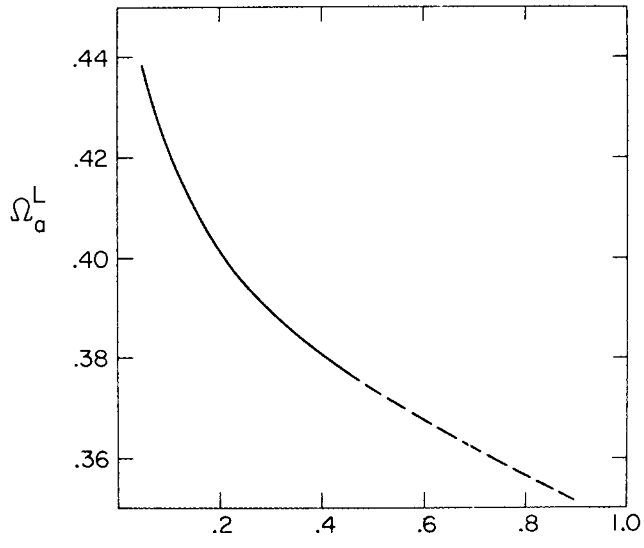

Fig. 4. Extrapolation of the dimensionless constant Ω_a^L in the Redlich-Kwong equation of state for saturated liquids.

Ω_a^L. In order to establish the required extrapolation, Ω_a^L was estimated by the use of generalized liquid density correlations (*5, 9*) for *n*-decane, *n*-dodecane, and *n*-heptadecane. The resulting plot of Ω_a^L versus ω is shown in Figure 4 with the extrapolation carried out to an acentric factor of approximately 0.9. These two parameters then permit the Poynting correction to be computed in exactly the same manner as the original correlation.

Liquid-Phase Fugacity

One of the main features of the C-P correlation is the unsymmetric convention for normalizing activity coefficients. Use of this convention, however, requires that binary data in the form of Henry's constants be available to define the standard state of supercritical components. Additional binary data, namely, self-interaction constants and dilation constants, are also required in the computation of activity coefficients by the dilated van Laar model.

Unlike the parameters that have been discussed up to this point, no convenient methods were available to estimate reliably these liquid-phase fugacity parameters for systems of petroleum fractions. In fact, the experimental phase equilibria data of petroleum fractions are so meager it is unlikely that any liquid solution model requiring binary data is feasible at the present time. In order to circumvent this lack of data, a modification had to be made to the original treatment of Chueh and Prausnitz.

The first step of this modification was to switch to a symmetric normalizing convention and define the standard state for all components as the pure liquid at a reference pressure of zero. Thus all pseudocomponents of the petroleum fraction are treated in essentially the same manner as the subcritical components of the original C-P correlation. While this standard state will be hypothetical for the low-boiling fractions, the generalized tables prepared by Lyckman, Eckert, and Prausnitz (*8*) provide the needed extrapolation up to a reduced temperature of 1.5.

The second step in the modification was to replace the dilated van Laar model for activity coefficients with a regular solution model (*6*). This substitution is ideally suited to systems of petroleum fractions for the very practical reason that pseudocomponent solubility parameters can readily be estimated. Furthermore, the solubility parameter has been found to be satisfactory in correlating phase equilibria data on hydrocarbons (*1*). Therefore the Chao-Seader treatment was adopted for the computation of liquid-phase activity coefficients.

$$RT \ln \gamma_i = v_i^L (\delta_i - \overline{\delta})^2 \tag{8}$$

$$\overline{\delta} = \frac{\sum_i x_i v_i^L \delta_i}{\sum_i x_i v_i^L} \tag{9}$$

$$\delta = \left(\frac{\Delta H_{v_i} - RT}{v_i^L} \right)^{1/2} \tag{10}$$

In these equations, δ_i is the solubility parameter of pseudocomponent i, $\overline{\delta}$ is the volume average solubility parameter of the liquid mixture, ΔH_v is the heat of vaporization, and v_i^L is the liquid molar volume. Similar to the approach used in the Chao-Seader correlation, δ_i and v_i^L were evaluated at 25°C. and were assumed to be a characteristic constant for each pseudocomponent.

Summary

The modified correlation presented here represents a hybrid between the original treatment of Chueh and Prausnitz and the Chao-Seader correlation. While the lineage may open to question, our main goal was to stay, as nearly as possible, within the framework of the C-P correlation rather than attempt an improvement in the Chao-Seader correlation.

The features retained from the original C-P correlation are the vapor-phase fugacity coefficient, the Poynting correction, and to some extent, a standard state fugacity at zero reference pressure. Features adopted from the Chao-Seader correlation are liquid-phase activity coefficients and the symmetric convention for normalizing activity coefficients.

TEST OF THE MODIFIED CORRELATION

One of the objectives of this work was to develop a modified C-P correlation for systems of petroleum fractions that was comparable in accuracy to the Chao-Seader cor-

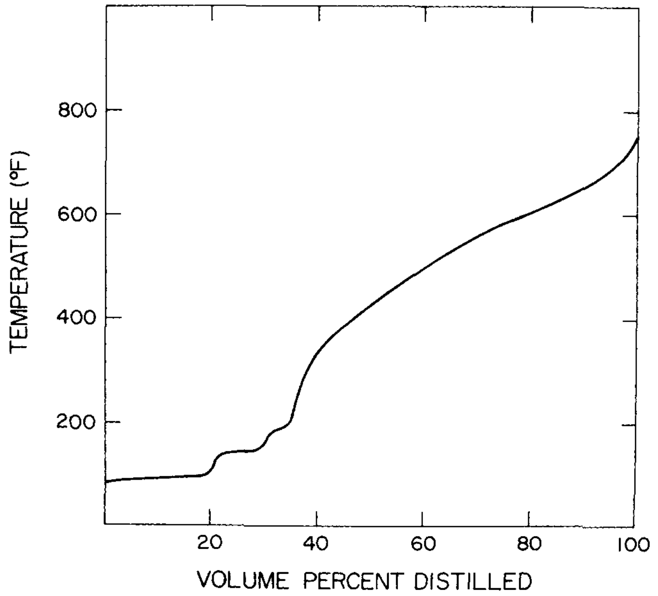

Fig. 5. True boiling point distillation of the naphtha-furnace oil blend used to test the modified C-P correlation [data of White and Brown (*13*)].

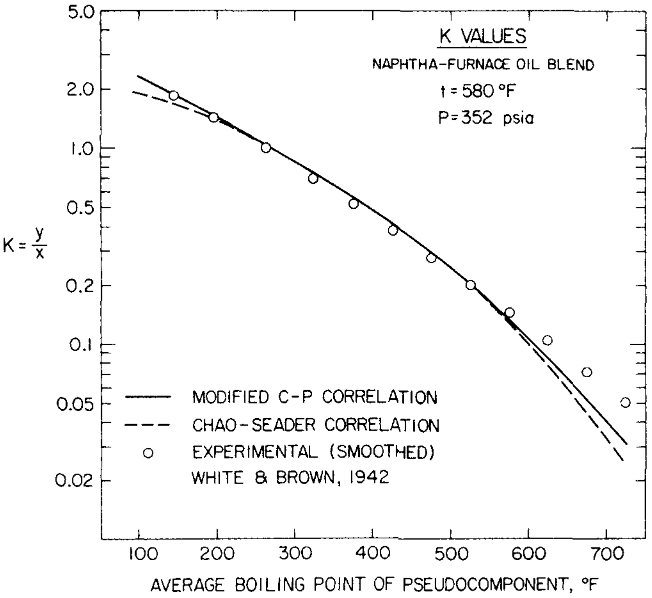

Fig. 6. Comparison between predicted and experimental *K* values at 580°F. and 352 lb./sq.in.abs.

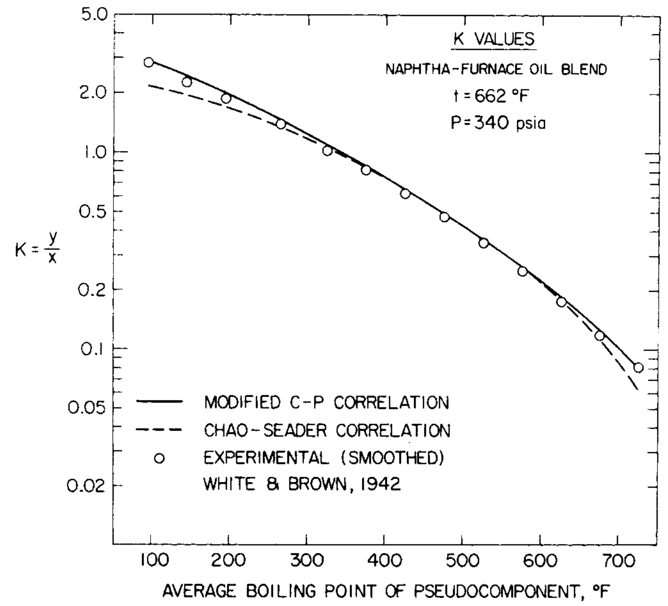

Fig. 7. Comparison between predicted and experimental *K* values at 662°F. and 340 lb./sq.in.abs.

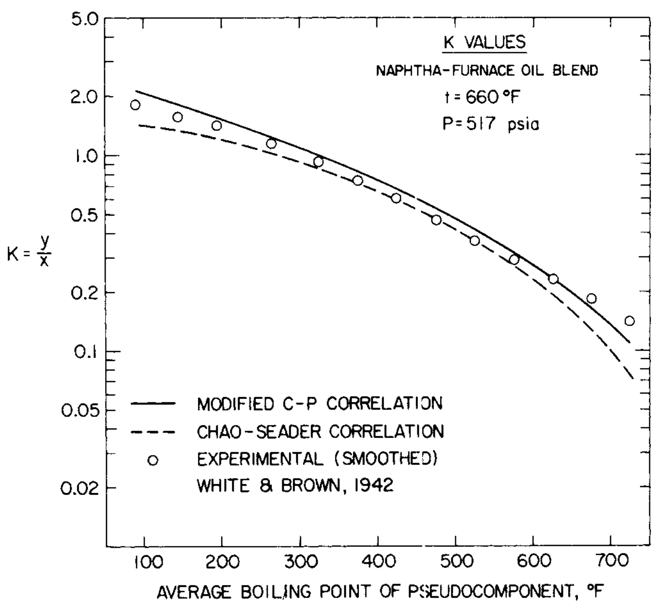

Fig. 8. Comparison between predicted and experimental *K* values at 660°F. and 517 lb./sq.in.abs.

relation. However, verification of this objective proved difficult due to the previously mentioned lack of experimental phase equilibria data. A survey of the bibliography compiled during the preparation of the API Technical Data Book (*5*, *7*) showed that most of the reported experimental data on petroleum fractions were unusable because they lacked sufficient information to suitably characterize the feed stocks or the flashed vapor and liquid streams. Of the data that were available, those of White and Brown (*13*) were selected as being the most suitable for testing the proposed correlation.

The feed stocks investigated by White and Brown were blends of light naphtha and furnace oil. Their mixture B was selected for this test and consisted of 35% by volume of naphtha and 65% by volume of furnace oil. The TBP distillation of this resulting petroleum fraction is shown in Figure 5.

As reported by White and Brown, the naphtha consisted of pentanes, hexanes, and heptanes, and the furnace oil had a boiling range of 180° to 750°F. To facilitate comparison of *K* values, the TBP distillation curve was divided into the same pseudocomponents as used in the original study (*13*). In addition to boiling points, specific gravity and molecular weight data were available to characterize each of the pseudocomponents. The other physical parameters, that is, critical properties, acentric factors, heats of vaporization, etc., were estimated via appropriate correlations in the API Technical Data Book (*5*). The important pseudocomponent characterizing parameters are summarized in Table 2.

As a representative sample of the experimental conditions, three states were selected for the test: 580°F. and 352 lb./sq.in.abs., 662°F. and 340 lb./sq.in.abs., and 660°F. and 517 lb./sq.in.abs. *K* values were computed by both the proposed correlation and the Chao-Seader method. These predicted *K* values were then compared with the smoothed experimental data reported by White and Brown. The results of this comparison are shown in Figures 6, 7, and 8, and are summarized in Table 3.

DISCUSSION

The results of these test calculations show that the modified correlation is indeed comparable in accuracy with the Chao-Seader method. Based on a total of 39 data points, the Chao-Seader correlation showed an average absolute deviation of 12.4%, while our modified C-P method gave a deviation of 9.1%. Equally important, as shown in Table 3, is the improvement in the maximum deviation.

In trying to speculate on possible reasons for this improvement, we observed that the vapor-phase fugacity coefficients predicted for the light components were approximately equal for both methods. However, as the pseudocomponent boiling points increased, the values of

TABLE 2. CHARACTERISTIC PARAMETERS FOR PSEUDOCOMPONENTS OF THE NAPHTHA-FURNACE OIL FEEDSTOCK

No.	Boiling range, °F.	Volume % of feed	Average boiling pt., °F.	Specific gravity @ 60°F.	Molecular weight	Acentric factor
1	86 to 95	21.5	92	0.632	72	0.220
2	135 to 156	8.6	145	0.683	86	0.280
3	175 to 209	5.3	195	0.728	97	0.315
4	209 to 300	1.6	266	0.748	115	0.400
5	300 to 350	3.0	328	0.762	134	0.450
6	350 to 400	6.6	377	0.775	150	0.500
7	400 to 450	6.1	425	0.789	168	0.550
8	450 to 500	7.1	476	0.804	187	0.597
9	500 to 550	7.5	526	0.819	208	0.655
10	550 to 600	11.1	577	0.835	231	0.718
11	600 to 650	10.7	622	0.851	257	0.762
12	650 to 700	6.8	672	0.867	286	0.829
13	700 to 750	4.1	723	0.884	320	0.879

TABLE 3. COMPARISON OF PREDICTED *K* VALUES

	Average deviation (% absolute)		Maximum deviation (% absolute)	
	Modified C-P	Chao-Seader	Modified C-P	Chao-Seader
580°F., 352 lb./sq. in. abs.	10.1	14.9	37.8	54.2
662°F., 340 lb./sq. in. abs.	5.2	8.5	7.8	27.1
660°F., 517 lb./sq. in. abs.	12.0	13.9	23.0	44.6
Overall	9.1	12.4	——	——

φ_i predicted by the modified treatment were progressively lower than those of the Chao-Seader correlation. This effect, which is most likely related to the difference in the dimensionless constants in the Redlich-Kwong equation, tended to increase the predicted K values and bring them into closer agreement with the experimental data.

The situation with regard to the liquid phase is less clear since both methods use the same regular solution activity coefficients. In the Chao-Seader philosophy, liquid-phase fugacities are given by

$$\hat{f}_i^L(P) = x_i\gamma_i(P)\, f_i^L(P) \qquad (11)$$

where the regular solution activity coefficient is defined relative to the fugacity of pure liquid i at the system pressure, P. The terms on the right-hand side of this equation can be converted to an arbitrary reference pressure P^r by making the following substitutions:

$$f_i^L(P) = f_i^L(P^r) \exp\left[v_i^L\,(P - P^r)/RT\right] \qquad (12)$$

$$\gamma_i(P) = \gamma_i(P^r) \exp\left[(\bar{v}_i^L - v_i^L)(P - P^r)/RT\right] \qquad (13)$$

In these equations the pure component liquid volume v_i^L and the partial liquid volume $\bar{v}_i^L$ have been assumed to be independent of pressure. However, according to the formal development of regular solution theory, $v_i^L = \bar{v}_i^L$. Therefore, after substitution, Equation (11) reduces to

$$\hat{f}_i^L(P) = x_i\gamma_i(P^r)\, f_i^L(P^r) \exp\left[v_i^L\,(P - P^r)/RT\right] \qquad (14)$$

Note that the Poynting correction in Equation (14) contains the volume of pure liquid i. Thus, when this equation is used for supercritical components, the usual problem of hypothetical liquid volume occurs. In the Chao-Seader correlation, this problem is handled by essentially treating the terms $f_i^L(P^r) \exp[v_i^L\,(P - P^r)/RT]$ to be an empirically determined function of temperature, pressure, and component acentric factor.

This problem of hypothetical liquid volumes can be sidestepped by adopting a slightly different viewpoint of the activity coefficient. Since regular solution theory requires that γ be independent of pressure, we consider the activity coefficient to be defined relative to the fugacity of pure liquid i at some fixed reference pressure P^r

$$\gamma_i(P^r) = \frac{\hat{f}_i^L(P^r)}{x_i\, f_i^L(P^r)} \qquad (15)$$

In terms of the system pressure, the liquid-phase fugacity is

$$\hat{f}_i^L(P^r) = \hat{f}_i^L(P) \exp\left[\bar{v}_i^L\,(P^r - P)/RT\right] \qquad (16)$$

Combining Equations (15) and (16) gives the following result:

$$\hat{f}_i^L(P) = x_i\gamma_i(P^r)\, f_i^L(P^r) \exp\left[\bar{v}_i^L\,(P - P^r)/RT\right] \qquad (17)$$

Unlike Equation (14), the Poynting correction in Equation (17) presents no difficulties with supercritical components and therefore was adopted in our modified C-P correlation.

Even with this approach to liquid-phase activity coefficients, the problem of hypothetical states is not completely eliminated. The pure component reference fugacity $f_i^L(P^r)$ must still be obtained by means of an extrapolated curve (*8*) for any component whose reduced temperature is greater than unity. While any such extrapolation is open to question, the result of this treatment is to reduce the general problem of hypothetical states to a single, identifiable term.

There is little doubt that the use of Henry's constants and an unsymmetric normalizing convention is superior to a hypothetical liquid treatment of supercritical components. What remains, however, is to develop a reliable method for estimating these binary parameters. Correlations such as those suggested by Prausnitz and Shair (*10*) and Yen and McKetta (*14*) may eventually resolve this dilemma.

ACKNOWLEDGMENT

We express our appreciation to Dr. A. E. Ravicz of Chevron Research Company, Richmond, California, for providing the computed results from the Chao-Seader correlation.

NOTATION

a, b = constants in the Redlich-Kwong equation
f = pure component fugacity
f^0 = reference fugacity
$\hat{f}$ = fugacity of component in a mixture
ΔH_v = heat of vaporization
K = equilibrium vaporization constant, K value
k_{ij} = characteristic constant for the i-j interaction
n = exponent in Equation (6)
N = number of components
P = total pressure
P^r = constant reference pressure
P_c = critical pressure
R = gas constant
T = temperature
T_c = critical temperature
T_{cij} = critical temperature characteristic of i-j interaction
U_i = UOP characterization factor of component i
U_{pi} = UOP characterization factor of a paraffin having the same boiling point as component i
v = molar volume
v_c = critical volume
$\bar{v}$ = partial molar volume
x = mole fraction in the liquid phase
y = mole fraction in the vapor phase

Greek Letters

γ = liquid-phase activity coefficient
δ = solubility parameter
φ = fugacity coefficient of component in a gas mixture
ω = acentric factor
Ω_a, Ω_b = dimensionless constants in the Redlich-Kwong equation

Superscripts

L = liquid phase
(P^r) = at constant reference pressure
o = reference state
V = vapor phase

Subscripts

c = critical
i = component i
ij = i-j interaction

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Turbulent Momentum Transfer in Two-Phase Cylindrical Couette Flow

RAVI GANDHI and JOSEPH ESTRIN

Clarkson College of Technology, Potsdam, New York

Torque measurements were made in experiments carried out using a cylindrical Couette apparatus with the inner cylinder rotating and the outer one stationary. The fluid systems employed consisted of distilled water, 50% distilled-water glycerine solutions, and these with several concentrations of suspended polystyrene spheres (through 40 on 70 mesh). The parameters employed by Bjorklund and Kays were found to correlate the data successfully when suspension viscosities were used for the two-phase systems.

This paper discusses momentum transfer processes which occur in two-phase turbulent systems of polystyrene spheres in distilled water and 50% distilled water-glycerine solutions flowing between a rotating inner cylinder and a stationary outer one. This geometry has been utilized in the past for studies of transport processes, usually in single-phase systems, so that its utilization as a chemical engineering research tool for studies of more complex multiphase systems has not been fully explored.

The use of a cylindrical Couette flow apparatus as a device for investigating complex two-phase phenomena would appear to have several advantages:

1. The process is confined in a simple, well-defined geometry.
2. Large heat transfer surface to volume ratio ensures good temperature control characteristics.
3. At high rotational velocities, the bulk of the homogeneous phase is practically uniform in temperature and concentration.
4. Minor density differences in the phase present would be ineffective in causing a classification of the phase because of the three-dimensional vortices which exist.

The first item states an obvious advantage over other commonly used devices such as stirred tanks making use of turbine—or propeller—impeller devices. Item 2 also implies an advantage in control and operation over the more standard mixer-tank apparatus. The last two items are tantamount to stating that mixing of the phases takes place very efficiently.

Two disadvantages associated with an apparatus of this type are

1. The fluid flow patterns are very complicated so that the interpretation of transport measurements for predicting phenomena in equipment with more standard geometries becomes a questionable procedure.
2. Effects due to large differences in densities of the phases are difficult to avoid; with the axis of the apparatus vertical, axial gradients of the suspended phase would readily occur.

This second item represents a major disadvantage, and heterogeneous systems in which density differences are large may not be considered for use in the Couette apparatus. However this fails to preclude possible use of this apparatus for such diverse processes as are included in liquid-liquid and many solid-liquid contacting operations.

From the foregoing it is apparent that a justifiable investigation into the general, potential use of the cylindrical Couette flow apparatus as a research tool involves a study of the nature of the fluid mechanics of turbulent flows in the annular space. A stationary outer wall is employed so that glass or a transparent polymeric material is readily used for the outer cylindrical container to enable observations of the interior.

Taylor (*14*) initiated much of the current interest in the cylindrical Couette geometry by predicting the critical speed at which instability sets in. He also demonstrated the existence of Taylor vortices which occur when the critical speed has been exceeded. Later Kaye and Elgar (9) showed that the Taylor number is an especially useful parameter in Couette flow studies. Taylor's expression for the critical speed, given explicitly for the critical Taylor number, with only the inner cylinder rotating, is