Liquid Phase Activity Coefficients and Standard State Hypothetical Liquid Fugacities for Hydrocarbons

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One method of predicting vaporization equilibrium ratios for the components of a multicomponent mixture is through the use of standard state liquid fugacities, standard state vapor fugacities, liquid phase activity coefficients, and vapor phase activity coefficients. The relationship among these variables will be shown.

It is the purpose of this paper to present a method for evaluating the fugacities of the components of a multicomponent liquid mixture which is in equilibrium with its vapors; to present a method for evaluating the standard state fugacities of hypothetical liquids and to disclose these values for methane and ethane up to a reduced temperature of 1.6 and values for propane up to a reduced temperature of 1.3; to present the coincident derived values of the vaporization equilibrium constants, Z factors, and solubility parameters; and to show correlations of these values.

The following definitions apply to the nonideal behavior of liquids and vapors:

$$\gamma_i^L = \frac{(f_i)_L}{(f_i^o)_L\, x_i} \tag{1}$$

and

$$\gamma_i^v = \frac{(f_i)_v}{(f_i)_v\, y_i} \tag{2}$$

When the vapors and the liquid of a multicomponent mixture are in equilibrium at a given temperature and pressure, $(f_i)_L$ and $(f_i)_v$ are equal. At equilibrium then through Equations (1) and (2)

$$K_i' = \frac{y_i}{x_i} = \frac{(f_i^o)_L}{(f_i^o)_v}\,\frac{\gamma_i^L}{\gamma_i^v} \tag{3}$$

The ratio of the standard state fugacities is usually expressed as

$$K_i = \frac{(f_i^o)_L}{(f_i^o)_v} \tag{4}$$

and is named the *vaporization equilibrium constant.* Equation (3) is frequently written as

$$K_i' = K_i\,\frac{\gamma_i^L}{\gamma_i^v} \tag{5}$$

Mertes and Colburn (*1*) and Scheibel (*2*) have used a term Z which is defined as

$$Z_i = \frac{(f_i^o)_v/P}{(f_i^o)_L/P_{vi}} = \frac{P_{vi}/P}{K_i} \tag{6}$$

Applying this definition to Equation (3) one gets

$$K_i' = \frac{\gamma_i^L}{\gamma_i^v}\,\frac{1}{Z_i}\,\frac{P_{vi}}{P} \tag{7}$$

It should be noted that the first two terms on the right-hand side of Equation (7) account for all deviations from ideality, because for the ideal situation the vaporization equilibrium ratio for a component is equal to the ratio of the vapor pressure of the component at the system temperature to the total pressure of the system.

Examination of Equations (1) through (7) shows that the problem of evaluating the equilibrium ratio for a component in a multicomponent mixture by means of Equation (7) may be resolved into five parts: the vapor pressure of the component at system temperature, the standard state vapor fugacity of the component at system temperature and total pressure, the standard state liquid fugacity of the pure component at system temperature and total pressure, the vapor phase activity coefficient of the component, and the liquid phase activity coefficient of the component.

Values for the vapor pressure may be readily obtained unless the component under consideration is above its critical temperature. If the component is above its critical temperature, satisfactory values for the hypothetical vapor pressure may be obtained by extrapolating the vapor-pressure curve into the supercritical region. As a part of the work presented here vapor pressures have been calculated for methane, ethane, propane, *n*-pentane, and *n*-octane in the supercritical region by means of the Antoine equation. Constants for this vapor pressure equation were obtained from Dreisbach (*3*). The vapor pressures were plotted on a log-log reference substance plot with *n*-octane as the reference component. Straight lines intersecting at a common vapor pressure of 103,000 lb./sq. in. abs. were obtained. It is not within the scope of this paper to discuss standard state vapor fugacities and vapor phase activity coefficients.

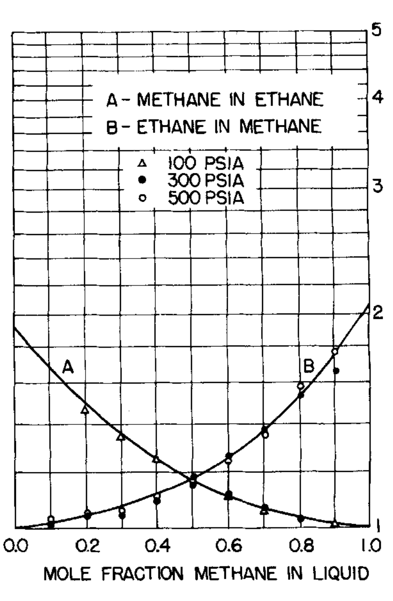

Fig. 4. Liquid phase activity coefficients in the methane-ethane system.

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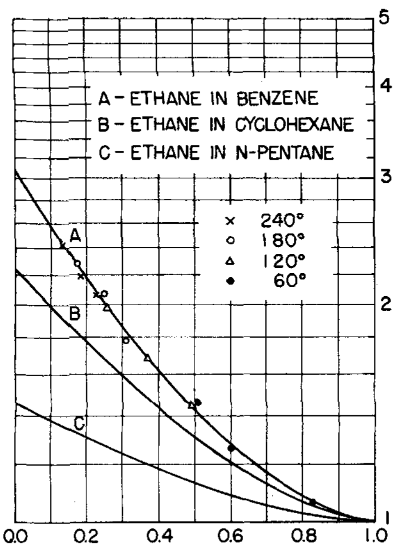

Fig. 6. Liquid phase activity coefficients of ethane in ethane-benzene, ethane-cyclohexane, and ethane-*n*-pentane systems.

FUGACITY OF COMPONENTS IN A MIXTURE

The fugacities of the components of a multicomponent liquid mixture at a given temperature and pressure may be evaluated by the use of the composition of the vapors in equilibrium with the liquid. The fugacity of each component of the vapors may be calculated; then the fugacity of each component in the liquid is equal to the fugacity of that component in the equilibrium vapor.

Black (*4*) has presented a method of evaluating the fugacity of a component in a multicomponent vapor mixture. His method is based on the following semiempirical equation of state of the van der Waals type:

$$(V_i)_v = \frac{RT}{P} + b_i - \frac{a_i \xi_i}{RT} \qquad (8)$$

His equation for the evaluation of the fugacity of a component of a multicomponent vapor mixture containing no polar compounds is

$$\ln \frac{(f_i)_v}{Py_i} = \frac{P}{RT}\left\{ b_i - \frac{a_i \omega_i}{RT} + \frac{\left(\sum_{j=1}^{n} G^{o}{}_{ij} y_j \right)^2}{RT} \right] \qquad (9)$$

where

$$G^{o}{}_{ij} = (a_i \xi_i{}^{o})^{0.5} - (a_j \xi_j{}^{o})^{0.5} \qquad (10)$$

$$\omega_i = \xi_i{}^{o} + \frac{0.0740}{T_r{}^4} P_{r_i} + \frac{0.0343}{T_r{}^5} P^2{}_{r_i} + \frac{0.0228}{T_r{}^6} P^3{}_{r_i} + 0.0442 \left(\frac{Py_i}{P_{v_i}} \right)^3 \qquad (11)$$

and

$$\xi_i{}^{o} = 0.396 + \frac{1.181}{T_r} - \frac{0.864}{T_r{}^2} + \frac{0.384}{T_r{}^3} \qquad (12)$$

In Equation (11)

$$P_{r_i} = \frac{Py_i}{P_{c_i}} \qquad (11a)$$

The authors have rewritten Equation (9) by introducing the terms σ and τ:

$$\frac{\left(\sum_{j=1}^{n} G^{o}{}_{ij} y_j \right)^2}{RT} = \{[(a_i \xi_i{}^{o})^{0.5} - (a_1 \xi_1{}^{o})^{0.5}]\, y_1 + [(a_i \xi_i{}^{o})^{0.5} - (a_2 \xi_2{}^{o})^{0.5}]\, y_2 + \text{-}\,\text{-}\, [(a_i \xi_i{}^{o})^{0.5} - (a_n \xi_n{}^{o})^{0.5}]\, y_n \}^2/RT \qquad (13)$$

$$\tau_i = \left[\frac{a_i \xi_i{}^{o}}{RT} \right]^{0.5} \qquad (14)$$

and

$$\tau_i{}^{+} = \left(\tau_i - \sum_{j=1}^{n} \tau_j y_j \right)^2 \qquad (15)$$

$$\sigma_i = \frac{a_i \omega_i}{RT} - b_i \qquad (16)$$

Consideration of Equations (9), (13), (14), (15), and (16) gives

$$\ln \frac{(f_i)_v}{Py_i} = \frac{P}{RT} (\tau_i{}^{+} - \sigma_i) \qquad (17)$$

With the temperature, pressure, and composition of a vapor mixture the fugacity of each component may be evaluated by Equation (17).

As a part of this work, to evaluate the fugacities of the several components of various multicomponent mixtures σ and τ values have been calculated for methane, ethane, propane, *n*-pentane, cyclohexane, and benzene. Values for methane and ethane are shown in Figures 1 to 3.* Note that σ is a function of both temperature and pressure, but τ is a function of temperature only.

In connection with the work presented here the vapor-liquid equilibrium data of Bloomer, Gami, and Parent (*5*) for the methane-ethane system; of Sage, Lacey, and Schaafsma (*6*) and Akers, Burns, and Fairchild (*7*) for the methane-propane system; of Sage and Lacey (*8*) for the propane-*n*-pentane system; of Glanville, Sage, and Lacey (*9*) for the propane-benzene system; of Reamer, Sage, and Lacey (*10*) for the ethane-*n*-pentane system; of Kay and Albert (*11*) for the ethane-cyclohexane system; and of Kay and Nevens (*12*) for the ethane-benzene system have been subjected to extensive thermodynamic analyses. Values for the fugacities of both components of these binaries have been calculated by means of Equation (17).

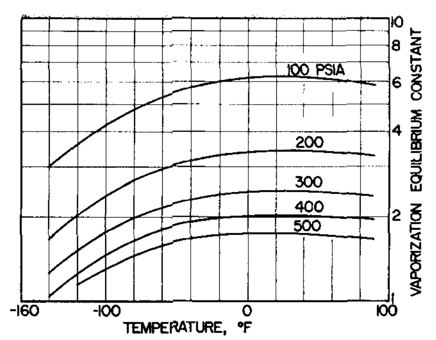

Fig. 10. Vaporization equilibrium constants of methane above the critical temperature.

The liquid phase activity coefficients for the less volatile component of each of the binaries studied were calculated by Equation (1) with the fugacities described above. For these calculations values for the standard state liquid fugacities were obtained from the generalized data of Lyderson, Greenkorn, and Hougen (*13*). Note that for the less volatile component standard state liquid fugacities of real liquids are involved because the pressure of the system is always equal to or greater than the vapor pressure of the less volatile component.

STANDARD STATE FUGACITIES OF HYPOTHETICAL LIQUIDS

Generally accepted values for standard state fugacities of hypothetical liquids below their critical temperatures have been calculated by the equation

$$(f_i{}^{o})_L = (f_{P_v})_i \exp \left\{ \frac{(V_i)_L}{RT} [P - P_{v_i}] \right\} \qquad (18)$$

Previous values for standard state fugacities of hypothetical lquids above their critical temperatures have been

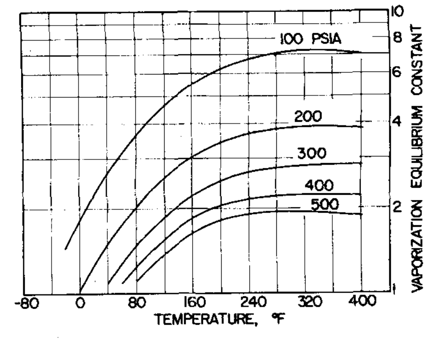

Fig. 11. Vaporization equilibrium constants of ethane above the critical temperature.

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* Figures 1, 2, 3, 5, 7, 8, 9, 15, and 16 as well as tables giving values of vaporization equilibrium constants and standard state liquid fugacities for methane, ethane, and propane have been deposited as document 7213 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $2.50 for photoprints or $1.75 for 35-mm. microfilm.

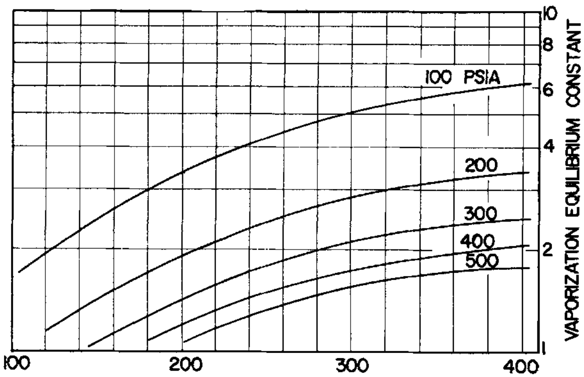

Fig. 12. Vaporization equilibrium constants of propane above the critical temperature.

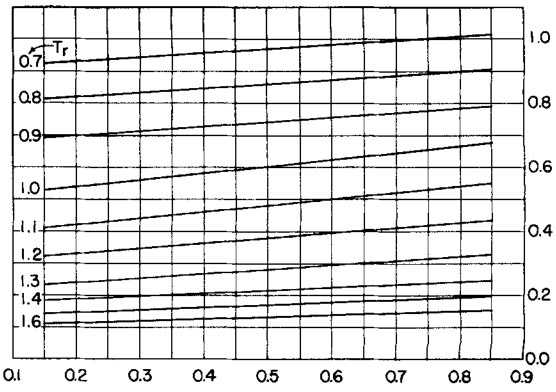

Fig. 13. Generalized correlation of $f^\circ{}_L/P_V$ values.

presented by Lewis and Kay (*14*); Souders, Selheimer, and Brown (*15*); Prausnitz (*16*); and Prausnitz, Edmister, and Chao (*17*).

The method used here to evaluate the standard state fugacities of hypothetical liquids is based on a solution of the Gibbs-Duhem equation, but the solution used depends upon information concerning the less volatile component.

A description has been given of how values of the liquid phase activity coefficients of the less volatile components of various binary mixtures were obtained. Then a modified form of the van Laar equation proposed by Black (*19*) was used. Black's equation is

$$\log \gamma_i = \frac{a_{ij}{}^2}{(1 + a_{ij}{}^2 x_i / a^2{}_{ji} x_j)^2} + E_i \tag{19a}$$

where

$$E_i = c_{ij} x_j \, (x_i - x_j) \, [3(x_i - x_j)\,(1 - x_i) + 2x_j] \tag{19b}$$

The constants $a^2{}_{12}$, $a^2{}_{21}$, c_{12}, and c_{21} were evaluated from the isothermal liquid phase activity coefficients of the less volatile component in the binary. With these constants the isothermal liquid phase activity coefficients of the more volatile component were calculated. Finally standard state fugacities for the more volatile component in the hypothetical liquid state were calculated by means of Equation (1).

Over the temperature and pressure ranges studied in this work all isothermal plots of $\log \gamma$ vs. x for a particular system were coincident. Furthermore the magnitude of E_i in Equation (19*a*) was negligible.

For the evaluation of the standard state fugacities for methane in the hypothetical liquid state, data from the methane-ethane system gave good values for liquid phase activity coefficients for ethane. From those values the coefficients $a^2{}_{ij}$ were evaluated, and liquid phase activity coefficients for methane were then calculated. Values for the standard state liquid fugacity were calculated from the liquid phase activity coefficients. This same procedure was repeated with the data for the methane-propane system used. The values of the standard state liquid fugacity for methane obtained from the two systems were adjusted to make them equal, but in so doing the activity coefficients were kept consistent with the modified van Laar equation. Figure 4 shows the liquid phase activity coefficients for the methane-ethane system. The solid lines represent the modified van Laar equation. The data points on the methane line are at temperatures below the critical and were obtained from Equation (1) by use of standard state hypothetical liquid fugacities which were calculated from Equation (18). Figure 5 shows the values for the standard state liquid fugacities of methane above the critical temperature.*

To calculate the standard state fugacities for ethane in the hypothetical liquid state the ethane-benzene system was used as the key system. Values of the liquid phase activity coefficient for benzene were evaluated, the constants for the modified van Laar equation were found, liquid phase activity coefficients for ethane were calculated, and the standard state liquid fugacities for ethane in the hypothetical liquid state were obtained. The standard state fugacity values were adjusted to make the activity coefficients for ethane in *n*-pentane, ethane in cyclohexane, and ethane in benzene all consistent with the modified van Laar equation. Figure 6 shows these activity coefficients. Temperature points are shown on the plot of $\log \gamma$ vs. x for ethane in benzene. The data points were evaluated from Equation (1) with the final values for the standard state fugacity. The 60°F. points are below the critical, while the other points represent values in the supercritical region. Figure 7 shows the values for the standard state liquid fugacities of ethane above the critical temperature.*

For the calculation of the standard state fugacities for propane in the hypothetical liquid state the propane-benzene system was used as the key system, and the propane-*n*-pentane system was used to make adjustments. Figure 8 shows the final values.*

The $a^2{}_{ij}$ coefficients for all of the binary systems which were studied are listed in Table 1.

Table 1. Constants of the Modified Van Laar Equation for the Binary Systems Studied*

System	$a^2{}_{12}$†	$a^2{}_{21}$**
Methane-ethane	0.285	0.288
Methane-propane	0.609	0.500
Ethane-*n*-pentane	0.167	0.216
Ethane-cyclohexane	0.356	0.487
Ethane-benzene	0.478	0.625
Propane-*n*-pentane	0.103	0.086
Propane-benzene	0.328	0.393

* Constant c_{ij} is zero for all systems.
† Component 1 is light component.
** Component 2 is heavy component.

DERIVED QUANTITIES

In order to test the consistency of the values of standard state fugacities for methane, ethane, and propane in the hypothetical liquid state above the critical temperatures with those values for the subcritical region, solubility parameters were calculated.

The solubility parameters for the methane, ethane, and propane in the supercritical region were calculated through use of the following equation:

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* See footnote on page 509.

* See footnote in column 2.

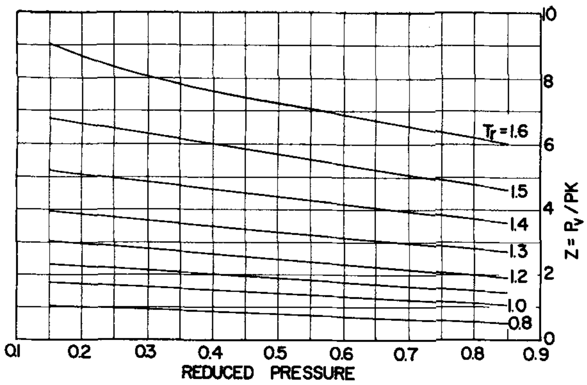

Fig. 14. Generalized correlation of Z values.

$$\delta_m = \delta_i - \left[\frac{RT \ln \gamma^L{}_m}{(V_m)_L \, x^2{}_{vi}} \right]^{\frac{1}{2}} \qquad (20)$$

Figure 9 shows the solubility parameters.* The solid lines represent values in the subcritical regions. The data points represent values in the supercritical region calculated with Equation (20).

For convenience in comparing the values presented here for standard state fugacities of liquids above their critical temperatures with previously used values, they have been converted to vaporization equilibrium constants by means of Equation (4). Values for the standard state vapor phase fugacities were calculated with Equations (15) and (17). For a pure component these equations reduce to

$$\ln \frac{(f_i^\circ)_v}{P} = \frac{P}{RT} (-\sigma_i) \qquad (21)$$

Values for the vaporization equilibrium constants are shown in Figures 10 to 12.

CORRELATIONS

Ehrett, Weber, and Hoffman (*21*) have shown that standard state liquid fugacities below the critical temperature may be generalized by plotting the $(f^\circ)_L/P_v$ ratio vs. reduced pressure with parameters of reduced temperature. The values for standard state liquid fugacities above the critical temperature obtained in this work have been likewise generalized by means of vapor pressure values described above. Lines of $(f^\circ)_L/P_v$ vs. P_r for reduced temperatures of 1.1, 1.2, 1.3, 1.4, and 1.6 have been added to previously prepared lines. This generalized plot is shown in Figure 13.

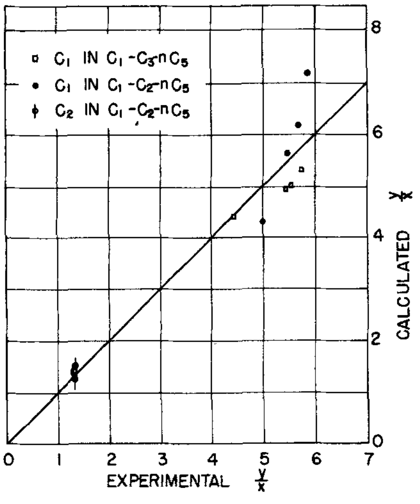

Fig. 17. Comparison of calculated and experimental y/x values at 100°F. and 500 lb./sq. in. abs.

The Z factor defined by Equation (6) for values below the critical temperature also has been generalized by Ehrett et al. (*21*). Values for Z above the critical temperature which were obtained in this work have been added to this generalized correlation. These values are shown in Figure 14. They are particularly useful in the calculation of vaporization equilibrium ratios with Equation (7).

COMPARISON OF PREDICTED DATA WITH EXPERIMENTAL DATA

In order to rigorously test the values of standard state fugacities for liquids above the critical temperature which are presented here the vapor-liquid equilibrium data of Billman, Sage, and Lacey (*22*) for the methane-ethane-*n*-pentane system and of Carter, Sage, and Lacey (*23*) for the methane-propane-*n*-pentane system have been examined. Specifically the data at 100°F. and 500 lb./sq. in. abs. were used.

Values of the fugacity for each component in the liquid mixtures were evaluated by Black's method (*24*). The $a^2{}_{ij}$ values for each of the binary pairs in the ternary mixtures were used to calculate the liquid phase activity coefficients of each component in the ternary by means of the following equation:

$$\log \gamma_i = [\sum_j a_{ij} \, r_{j2} \, x_j / \sum_k x_k \, r_{k2}]^2 \qquad (22a)$$

where

$$r_{ij} = a^2{}_{ij} / a^2{}_{ji} \qquad (22b)$$

The $a^2{}_{ij}$ values for methane-*n*-pentane were evaluated by

$$a_{13} = a_{12} - a_{23} \, r_{12}^{\frac{1}{2}} \qquad (23)$$

The values of the fugacity of each component in the liquid mixtures were then calculated by Equation (1). Note that the $a^2{}_{ij}$ values depend upon the standard state liquid fugacity values, and, more important, note that the values of the fugacity for a particular component in the liquid mixtures depend directly upon the standard state liquid fugacity values for that component.

Values of the fugacity for each component in the vapor mixtures were evaluated from values of $(f_i)_v/Py_i$ which were calculated by Equation (17).

A proof of the reliability of the methods described here for evaluating the fugacities of components in liquid mixtures and the fugacities of components in vapor mixtures lies in the fact that, for vapor-liquid equilibrium data, the fugacities of a component in the liquid and vapor phases must be equal. The methods have been shown to be reliable by comparing values of the liquid phase and vapor phase fugacities for *n*-pentane at four data points in each of two ternary mixtures. These values are shown in Figure 15.* At 100°F. *n*-pentane is well below its critical temperature, and therefore values of standard state liquid fugacities are known to be correct. The values of fugacity in the liquid and vapor phases for propane and ethane in the two ternaries at 100°F. have been found to compare favorably. In these cases propane is below its critical temperature and ethane is slightly above its critical temperature.

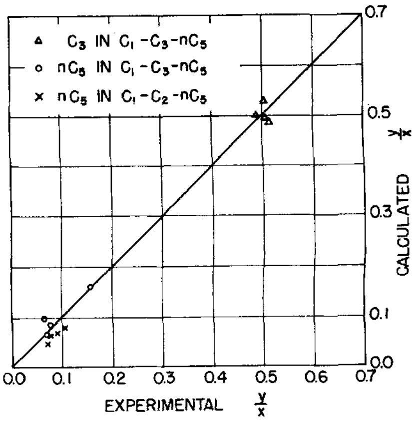

Fig. 18. Comparison of calculated and experimental y/x values at 100°F. and 500 lb./sq. in. abs.

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* See footnote on page 509.

* See footnote in column 1.

With the reliability of the methods for calculating the fugacities of components in the liquid and vapor phases established, the validity of the standard state liquid fugacity values for methane above its critical temperature was proven by the good comparison of liquid phase fugacities with vapor phase fugacity values for methane in the two ternaries. A comparison of these values is shown in Figure 16.* Another test of the validity of the standard state liquid phase fugacity values presented here compares the vaporization equilibrium ratio values predicted from Equation (7) with experimental values. This comparison is shown in Figures 17 and 18.

DISCUSSION AND CONCLUSION

The values of standard state fugacities for hypothetical liquids above the critical temperatures presented in this work are less than values reported by Lewis and Kay (*14*) and by Souders et al. (*15*). This is to be expected because for all pressures below the vapor pressure the exponential term in Equation (18), which was neglected by Lewis and Kay (*14*), is less than unity. Also in the case of values from Souders et al. (*15*) examination of Equation (5) shows that the assumption that the liquid phase is ideal would result in values of standard state liquid fugacities which are too large. The values obtained in this work are consistent with the liquid phase activity coefficients for various ethane systems as derived by Prausnitz (*16*). However at temperatures above the critical these values differ considerably from those presented by Prausnitz et al. (*17*).

The values presented in this work have been subjected to rigorous tests for thermodynamic consistency and validity, and they have been found to be reliable values for use in the prediction of the vaporization equilibrium ratios of the components of multicomponent mixtures. The method elucidated here may be used to obtain standard state hypothetical liquid fugacities for other components.

ACKNOWLEDGMENT

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NOTATION

a = van der Waals' attraction constant
a^{*} = coefficient in modified van Laar equation
b = van der Waals' covolume constant
c = empirical coefficient in modified van Laar equation
E = correction term in modified van Laar equation, defined by Equation (19*b*)
f = fugacity of a component in a mixture
f^{o} = fugacity of a pure component at a given temperature and pressure (standard state fugacity)
G^{o} = an attraction coefficient in Black's equation of state for mixtures
K = vaporization equilibrium constant, defined by Equation (4)
K' = vaporization equilibrium ratio, defined by Equation (3)
P = total pressure of a system
P_{r_i} = reduced partial pressure of component i in a mixture, defined by Equation (11*a*)
P_v = vapor pressure
r = coefficient in equation for activity coefficient in a multicomponent mixture, defined by Equation (22*b*)
R = gas law constant
T = absolute temperature
ΔU^v = change in internal energy accompanying vaporization
V = molar volume
V_ω = characteristic constant for a liquid
x = mole fraction in liquid phase
x_v = volume fraction in liquid phase
y = mole fraction in vapor phase
Z = vaporization equilibrium constant coefficient, defined by Equation (6)

Greek Letters

γ^L = liquid phase activity coefficient
γ^V = vapor phase activity coefficient
δ = solubility parameter
ξ = attraction coefficient in Black's equation of state
ξ^o = limiting value of ξ at zero pressure
σ = composition parameter dependent upon temperature and pressure, defined by Equation (16)
τ = attraction coefficient dependent upon temperature, defined by Equation (14)
τ^{+} = composition parameter dependent upon temperature, defined by Equation (15)

Subscripts

c = critical property
i, j, k = components in a mixture
l = less volatile component in a binary mixture
L = liquid phase
m = more volatile component in a binary mixture
P_r = saturated property
r = reduced property
v = vapor phase
1, 2, - - n = the components of a mixture

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* See footnote on page 509.