The Correlation of Vapor-Liquid Equilibria of Light Hydrocarbons in Paraffinic and in Aromatic Solvents at Low Temperatures and Elevated Pressures

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A correlational procedure was developed to predict the vapor-liquid equilibrium behavior of light hydrocarbons in heavier hydrocarbon solvents at low temperatures and elevated pressures. The method is applicable to paraffinic as well as aromatic solvents.

The method employed the Benedict-Webb-Rubin equation of state to predict the vapor phase fugacities. Methane liquid fugacities in the various hydrocarbon solvents were based upon Henry's law which included terms to account for compositional and pressure effects. The liquid fugacities for ethane and propane were calculated using infinite dilution data to modify empirically the Scatchard-Hildebrand equation. Excellent agreement between the correlated and low-temperature data available on this class of systems was obtained.

The literature abounds with correlations for vapor-liquid equilibria at elevated pressures. Of particular note are the Chao-Seader correlation (*4*), correlations in light hydrocarbon systems based on equations of state (*1*), and convergence pressure correlations such as those appearing in the NGSMA Data Book (*12*). The strength of the Chao-Seader correlation lies in its generality; that is, in its ability to predict vapor-liquid phase behavior in systems composed of paraffins, napthenes and aromatics, including gases such as hydrogen, nitrogen, carbon dioxide, and hydrogen sulfide at low concentrations. The application of equations of state and the corresponding states methods is usually limited to systems composed of paraffins and nonpolar substances. The purpose of this paper is to develop a method of predicting phase behavior in systems containing a supercritical component, methane, with intermediates, ethane and propane, and a relatively heavy paraffin or aromatic component, such as heptane or toluene, using basic data which are functions of pressure and temperature only. Temperatures of interest range from 70° to −100°F. and pressures up to 1,500 lb./sq. in. abs. Other correlations have not been successful for this type of system under these conditions.

By definition, the vapor-liquid equilibrium constant, or K value, is the ratio of mole fractions of the component in the vapor and in the liquid. Since the fugacities for components are equal among the equilibrium phases

$$K_i = (f_i^L/x_i)/(f_i^V/y_i) = [f_i^L/(x_iP)]/[f_i^V/(y_iP)] \quad (1)$$

Chao and Seader (*4*) chose to separate the liquid fugacity coefficient, $[f_i^L/(x_iP)]$, into two parts: one identified with the component and the other with liquid phase nonideality.

$$(f_i^L/x_iP) = (f_i^{oL}/P) \quad [f_i^L/(x_if_i^{oL})]$$

where f_i^{oL} = the fugacity of pure liquid i at system T and P.

The second term of the right-hand member is defined as the liquid phase activity coefficient and is

$$\gamma_i = [f_i^L/(x_if_i^{oL})] \quad (2)$$

where γ_i = activity coefficient of i in the liquid phase.

The first term of the right-hand side is the pure component fugacity coefficient of i in the liquid

$$\nu_i^o = f_i^{oL}/P \quad (3)$$

The problem encountered in applying the Chao-Seader approach to methane is that the temperatures of the systems studied are above the critical temperature of methane, requiring that ν_1° be calculated for a hypothetical liquid. Chao and Seader treated the liquid parameters in their equation for the gaseous component as empirical parameters and determined them from a fit of existing high-temperature experimental data. Application of their correlation to the low-temperature system methane–propane–*n*-heptane did not give satisfactory prediction of the phase behavior, as shown in Figures 1 and 2.

Experimental data are available to formulate and test correlational methods for light hydrocarbon-hydrocarbon solvent systems at low temperatures. Reviews of the data are presented elsewhere (*3, 15, 22*).

Recent binary references particularly pertinent to this paper are:

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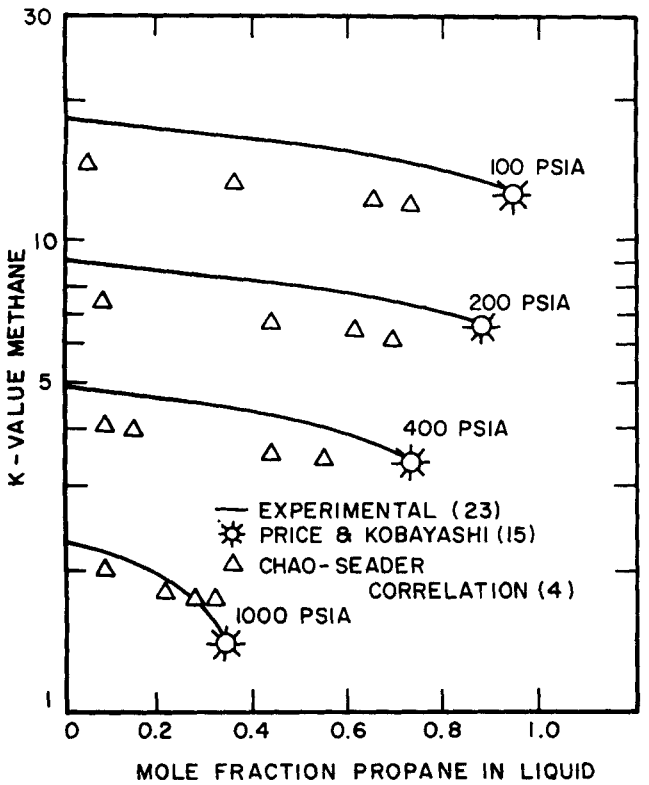

Fig. 1. Methane K value in the C_1–C_3–n-C_7 system. Comparison between experimental data and Chao-Seader correlation. $T = -40°F.$

System	Temperature	Reference
Methane–*n*-butane	−80° to 280°F.	(17)
Methane–*n*-hexane	−110° to 150°C.	(20)
Methane–*n*-octane	−110° to 150°C.	(7)
Methane–*n*-nonane	−25° to 75°C.	(21)
Methane–*n*-decane	−20° to 40°C.	(8)

The experimental work reported in a companion paper (23) presents the following information:

1. K values of methane and propane at finite concentrations in the methane–propane–*n*-heptane system and K values of ethane at vanishingly small concentrations (infinite dilution) in the system, for temperatures between 0° and −100°F. and pressures to 1,600 lb./sq. in. abs.
2. K values of methane and propane at finite concentrations and of ethane at infinite dilution in the methane–propane–toluene system at −40°F. and for pressures to 1,000 lb./sq. in. abs.
3. K values of methane and ethane in the methane–ethane–*n*-heptane system for −20°, −40°, and −60°F. and pressures to 1,600 lb./sq. in. abs.

This information was the principal experimental basis for this correlational effort.

METHANE CORRELATION

The hypothetical liquid standard state for methane can be circumvented by referring to the infinite dilution state of methane in the liquid as the standard state, rather than to the nonexistent pure methane liquid state.

$$f_1^{\infty} = \lim_{x_1 \to 0} f_1/x_1 \tag{4}$$

Defined in this manner, f_1^{∞}'s are also the Henry's law constants for methane in the various solvents.

The work of Kohn and co-workers (6, 7, 20, 21) and of Chang (2, 3) reveals that methane deviates only slightly from Henry's law, in binaries with heavy hydrocarbons, up to methane mole fractions of at least 0.2 and in some cases to $x_1 = 0.4$. Therefore an approach based on Henry's law was investigated as a means of correlating the methane K values.

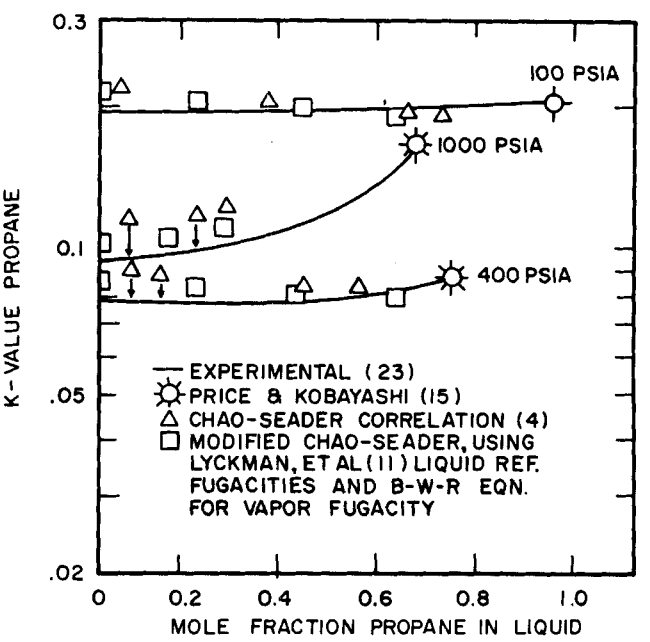

Fig. 2. Propane K value in the C_1–C_3–n-C_7 system. Comparison among experimental data, Chao-Seader correlation, and a modified Chao-Seader correlation. $T = -40°F.$

The following equation, reported by Prausnitz (14) and used by Orentlicher and Prausnitz (13) for hydrogen solubility in cryogenic solvents, was adopted:

$$\ln\left(\frac{f_1^L}{x_1}\right) = \ln \gamma_1^{\infty} f_1^{\infty} + \frac{\overline{V}_1^{\infty}}{(RT)} (P - P_0) \tag{5}$$

where γ_1^{∞} has been normalized so that $\lim_{x_1 \to 0} \gamma_1^{\infty} = 1$. P_0 is a low pressure where $\overline{V}_1 = \overline{V}_1^{\infty}$, $\gamma_1^{\infty} = 1$, and $f_1^L/x_1 = f_1^{\infty}$; that is, where component 1 is infinitely dilute.

Rigorously, P_0 would be the vapor pressure of the solvent at the system temperature. However, in many cases the vapor pressure is not known but is low enough to be negligible. P_0 was chosen as 1 atm. in this analysis. Equation (5) is also similar to the Krichevsky-Kasarnovsky equation (10), except for the inclusion of the activity coefficient γ_1^{∞}. By basing all fugacities on the same pressure P_0 and temperature T, an integrated form of the Gibb's-Duhem equation may be used for the activity coefficient. For example, Orentlicher and Prausnitz (13) used the single suffix Margules equation.

The methane binary systems observed also exhibited a linear dependence of $\ln f_1^{\infty}$ on $1/T$ for the low-temperature range of interest, which is represented as

$$\ln f_1^{\infty} = A + B/T \tag{6}$$

Evaluation of (f_1^L/x_1) from experimental data in the methane binary systems was made from the equation

$$\frac{f_1^L}{x_1} = K_1 \frac{f_1^V}{y_1 P} P \tag{7}$$

If $[f_1^V/(y_1P)]$ (the vapor phase fugacity coefficient of methane) can be determined, (f_1^L/x_1) can be calculated from the experimental methane K values and Equation (7). The Benedict-Webb-Rubin equation of state (1) was used to calculate the vapor phase fugacity coefficient, using published values of the hydrocarbon constants, with noted corrections in C_0 (1) at low temperature.

The only term of Equation (5) remaining to be determined is the partial molal volume of methane at infinite dilution $\overline{V}_1^{\infty}$. The effect of the pressure correction to fugacity (Poynting correction) in which $\overline{V}_1^{\infty}$ occurs is secondary. Therefore values of $\overline{V}_1^{\infty}$ need not be extremely accurate to

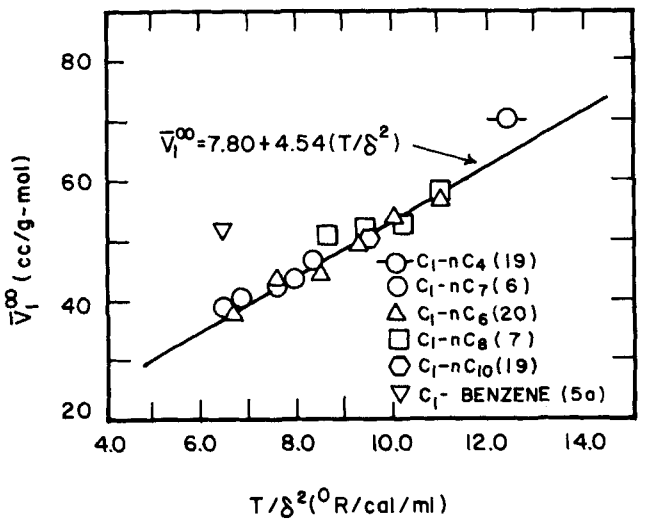

Fig. 3. Correlation of partial molar volume for methane at infinite dilution in hydrocarbon solvents.

give satisfactory results. For example, the total effect of the Poynting correction for (f_1^L/x_1) in methane–*n*-heptane at −80°F. and 1,000 lb./sq. in. abs. is approximately 14%. This is near the maximum correction applied to any fugacities used in this analysis. Lyckman et al. (*11*) proposed the correlation which was used here for $\bar{V}_1^{\infty}$. They obtained

$$\frac{\bar{V}_1^{\infty}P_{C_1}}{RT_{C_1}} = \text{function of } \frac{TP_{C_1}}{(\delta_2)^2T_{C_1}} \tag{8}$$

A plot for numerous gaseous solutes in different solvents revealed a linear relationship at temperatures reasonably below the mixture critical temperature (non expanded solvents). Since this work was concerned only with methane, a linear relation

$$\bar{V}_1^{\infty} = D_1 + D_2\,(T/\delta_2^2) \tag{9}$$

serves as well, for methane volumes only. D_1 and D_2 are tabulated in Table 2. Volumetric data were obtained by graphical differentiation of reported low-temperature liquid volume data (*19*, *6*, *20*, *7*) and are shown in Figure 3.

The analysis of the methane liquid fugacities calculated from experimental data and Equation (7) revealed a nearly linear dependence of $\ln \gamma_1^{\infty}$ on x_1. Examples are shown in Figure 14. It was recognized that this linear relation does not obey the Gibbs-Duhem relation, in general. However, the methane liquid compositions were restricted to values less than $x_1 = 0.5$ in this analysis, and thermodynamic consistency is possible with such a function in this restricted composition range.

Because $\ln \gamma_1^{\infty}$ appeared linear in x_1, the experimental data of each binary system was fit by a linear regression procedure to the following equation for the binary methane K values:

$$\ln\left(\frac{f_1}{x_1}\right)^L = A + \frac{B}{T} + \frac{C}{T}\,x_1 + \frac{\bar{V}_1^{\infty}}{RT}\,(P - P_0) \tag{10}$$

The data points for x_1 significantly greater than 0.5 were not included in the fit because the approach based on Henry's law is no longer valid. The results of the analysis are shown in Table 1, together with a list of systems studied and the temperatures considered. The pressure limits were established by the requirement that x_1 be less than 0.5. As indicated in Table 1, Equation (10) fits each individual system well, with resulting constants A, B, and C, depending upon the solvent in the system.

It is now necessary to relate the A, B, and C's to solvent characteristics. The Scatchard-Hildebrand equation was used to characterize the solvent. For methane at finite concentrations, the Scatchard-Hildebrand equation is (*5*)

$$RT \ln \gamma_1 = V_1 \phi_2^2\,(\delta_1 - \delta_2)^2 \tag{11}$$

where

$$\gamma_1 = f_1^L/(x_1 f_1^{\circ L})$$

The compositional dependence of γ_1 is included in ϕ of Equation (11). However, for $x_1 \longrightarrow 0$, $\phi \longrightarrow 1$ and only solvent characteristic effects remain. Therefore Equation (10) was forced to be consistent with the Scatchard-Hildebrand Equation (11) at $x_1 \longrightarrow 0$. The Scatchard-Hildebrand equation, Equation (11), reduces to

$$\{\ln f_1^{\infty} = A^1 + B^1\,(\delta_1 - \delta_2)^2\}_{T\ \text{constant}} \tag{12}$$

at small values of x_1, where A^1 and B^1 are empirical for a supercritical component such as methane and are functions of T only.

Equation (10) reduces to Equation (6) as $x_1 \longrightarrow 0$. Comparison of Equations (6) and (12) suggested the following functional forms of the A and B constants of Equation (10):

$$A = A_1 + A_2\,(\delta_1 - \delta_2)^2$$
$$B = B_1 + B_2\,(\delta_1 - \delta_2)^2$$

TABLE 1. DIRECT FIT OF EQUATION (10) TO INDIVIDUAL BINARY SYSTEMS CONTAINING METHANE*

Equation (10)

$$\ln(f_1/x_1) = A + B(T_{C_1}/T) + C(T_{C_1}/T)\,x_1 + [\bar{V}_1^{\infty}/(RT)]\,(P-1)$$

T_{C_1} = critical temperature of methane

System	Min. T, °F.	Max. T, °F.	A	B	C	No. of points	Average† absolute % error
Methane–propane	−100.0	50.0	6.8336	−2.7910	−0.96875	28	4.2
Methane–*n*-butane	− 80.0	100.0	6.9554	−2.8353	−0.61339	37	5.9
Methane–*n*-hexane	−103.0	32.0	7.1535	−2.8614	−0.65284	30	0.8
Methane–*n*-heptane	−100.0	40.0	7.1802	−2.9074	−0.58416	44	0.9
Methane–*n*-octane	− 58.0	32.0	7.2987	−2.9952	−0.55867	21	0.8
Methane–*n*-nonane	− 58.0	77.0	7.1750	−2.9182	−0.28970	42	2.2
Methane–*n*-nonane	− 58.0	32.0	7.3701	−3.1505	−0.32124	31	1.5
Methane–*n*-decane	− 20.0	100.0	6.8447	−2.5142	−0.06520	31	1.0
Methane–toluene	− 40.0	−40.0	‡	‡	−1.3325	8	1.5

*For $x_1 < 0.5$ mole fraction methane.

‡A and B not separately calculated at only one temperature. $A + B(T_{C_1}/T) = 5.6823$.

†Percent error $= \dfrac{K_{\text{corr.}} - K_{\text{exp.}}}{K_{\text{exp.}}}$.

These constants were fit in this manner to the data given in Table 1.

The parameter C is left to be correlated with solvent properties. It appeared from the data that deviations from Henry's law were related to the density of the solvent. The C's evaluated were not extremely regular and their effect was secondary. A linear fit of C to the molar density of the solvents calculated from the Chao-Seader (4) molar volumes at 25°C. was used to correlate the C's in the binary systems investigated.

The general correlation which resulted from the described analysis was

$$\ln \frac{f_1^L}{x_1} = A + \frac{B}{T} + \frac{C}{T} x_1 + \frac{\overline{V}_1^{\infty} (P - P_o)}{RT} \qquad (13)$$

where

$$A = A_1 + A_2 (\delta_1 - \delta_2)^2$$
$$B = B_1 + B_2 (\delta_1 - \delta_2)^2$$
$$C = C_1 + C_2/V_2$$
$$\overline{V}_1^{\infty} = D_1 + D_2 (T/\delta_2^2)$$

P_o was chosen as 1 atm., since solvent vapor pressures were not accurately known. At 1 atm. methane is at vanishingly small compositions in the liquid phase of the systems studied.

All values for solubility parameters were taken from Chao and Seader (4). The equation and the values of the constants used are given in Table 2.

The correlation of mixture data for methane was also possible from this equation. In the analysis of the binaries, each of the δ_2's (solvent solubility parameters) was evaluated for the pure solvent. At a given T, P in a more complex mixture, the methane-free liquid is analogous to the pure solvent in the binaries. Hildebrand and Scott (5) show that the solubility parameter of a mixture is formed from the values for the pure components by

$$\delta_M = \left(\sum_j x_j \delta_j V_j \right) \Big/ \left(\sum_j x_j V_j \right)$$

For a liquid solution of composition $(x_1, x_2, \ldots x_N)$ in which methane fugacity is to be calculated

$$\delta_M = \left(\sum_{i=2}^{N} x_i' \delta_i V_i \right) \Big/ \left(\sum_{i=2}^{N} x_i' V_i \right) \qquad (14)$$

where

$x_i' = x_i/(1 - x_1)$, mole fraction of i in methane-free liquid

The δ_M calculated in this manner becomes the δ_2 of Equation (13). V_2 for Equation (13) is the denominator of Equation (14).

K values are obtained for methane by use of Equations (1) and (13). The liquid fugacity (f_1^L/x_1) is calculated from Equation (13) and then the K value from Equation (1). The B-W-R equation of state was used to evaluate the vapor phase fugacity, $[f_1^V/(y_1 P)]$.

TABLE 2. CORRELATION FOR METHANE LIQUID FUGACITY, EQUATION AND CONSTANTS

Equation (13):

$$\ln(f_1^L/x_1) = \left(A_1 + B_1 \frac{T_{C_1}}{T}\right) + \left(A_2 + B_2 \frac{T_{C_1}}{T}\right)(\delta_1 - \delta_2)^2 + \left(C_1 + C_2 \frac{1}{V_2}\right) \frac{x_1 T_{C_1}}{T} + \left(D_1 + D_2 \frac{T}{\delta_2^2}\right) \left(\frac{P - P_0}{RT}\right)$$

T_{C_1} = 191.06°K. critical temperature of methane
T = temperature, °K.
f_1^L = partial fugacity of methane in liquid, atm.
P_o = reference pressure, defined as 1 atm.
δ_1 = solubility parameter of methane (cal./cc.)$^{1/2}$
δ_2 = solubility parameter of solvent (cal./cc.)$^{1/2}$
x_1 = mole fraction methane in liquid
A_1 = 6.8157
A_2 = 0.12967 (cal./cc.)$^{-1}$
B_1 = −2.8371
B_2 = −0.027579 (cal./cc.)$^{-1}$
C_1 = −0.1350
C_2 = −71.27 (cc.)
D_1 = 7.80 (cc.)
D_2 = 8.17 (cal./°K.)

Component	(cal./cc.)$^{1/2}$	V (cc.) from Chao-Seader (4)
Methane	5.68	52.0
Ethane	6.05	68.0
Propane	6.40	84.0
n-Butane	6.73	101.4
n-Hexane	7.27	131.6
n-Heptane	7.430	147.5
n-Octane	7.551	163.5
n-Nonane	7.65	179.6
n-Decane	7.72	196.0
Toluene	8.92	106.8

DEVELOPMENT OF A CORRELATION FOR THE INTERMEDIATE COMPONENTS

Ethane and propane K values calculated directly from the Chao-Seader correlation (4) were investigated. Consistently high results were obtained for propane at low temperatures. This was attributed to inaccuracies in their correlation of ν_i^o, the pure component fugacity coefficient. The generalized reference fugacities of Lyckman et al. (11) for the liquid were then used in conjunction with the B-W-R equation for vapor fugacity coefficients. The results were generally only slightly improved. Figure 2 shows the comparison of each of these methods with experimental data and reveals the incorrect qualitative behavior of ethane and propane K values calculated in this manner. The high value at infinite dilution was attributed to a high value of the activity coefficient predicted by the Scatchard-Hildebrand equation.

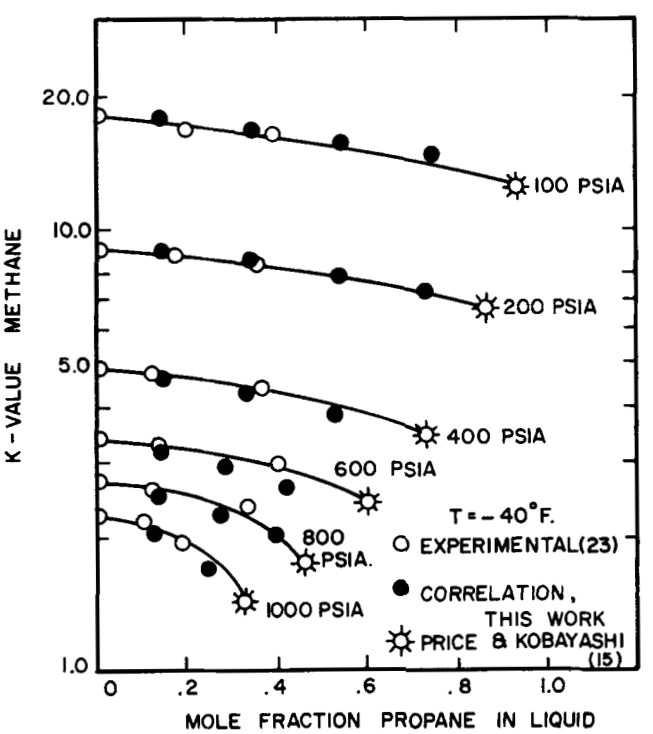

*Fig. 4. Methane K value in the C_1–C_3–*n*-C_7 system. $T = -40°F.$*

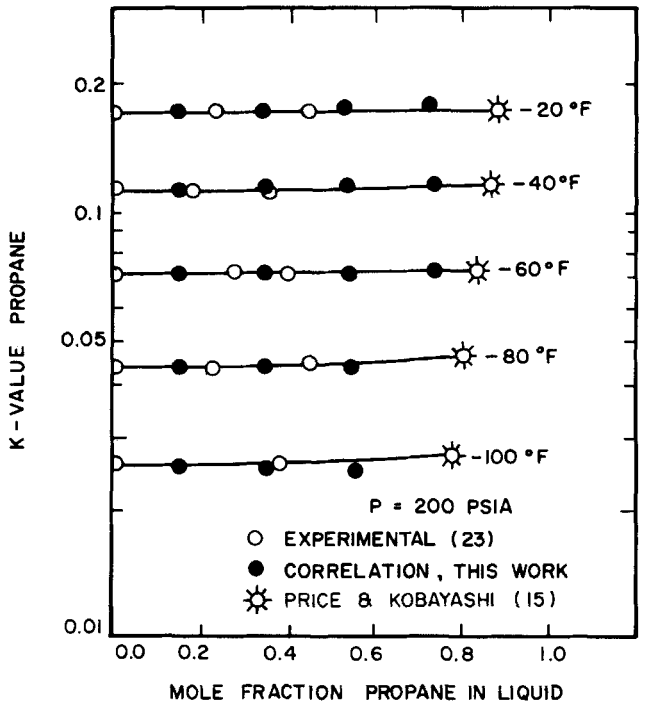

Fig. 5. Propane K value in the C_1–C_3–n-C_7 system. P = 200 lb./sq.in.abs.

The principal failings of the Chao-Seader correlation as applied to ethane and propane in the systems studied are its improper prediction of compositional effects in paraffin systems. It does show the correct qualitative behavior in the methane-propane-toluene system, where extreme compositional effects occur. The Scatchard-Hildebrand equation does not account for size effects which occur in the paraffin systems studied. Predicted activity coefficients for ethane and propane at low concentrations in long chain paraffin solvents are greater than 1. The true activity coefficients are less than 1 in these systems due to size difference between solute and solvent molecules.

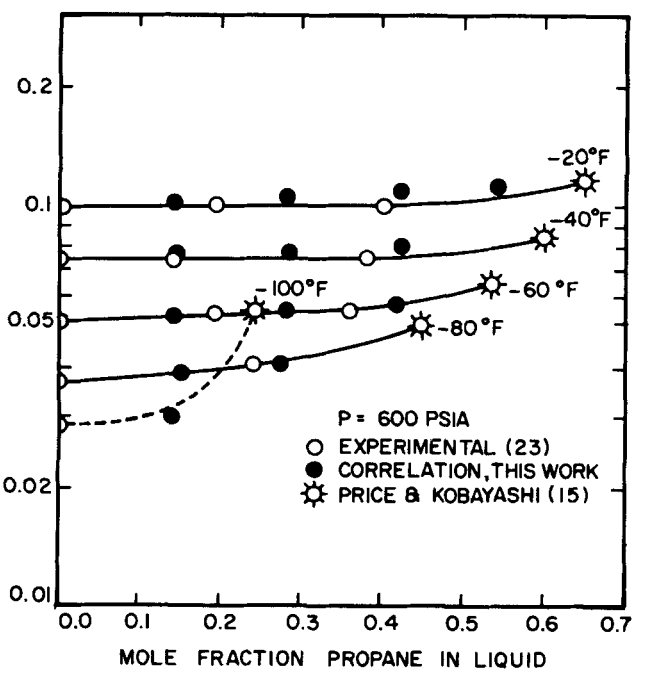

Fig. 6. Propane K value in the C_1–C_3–n-C_7 system. P = 600 lb./sq.in.abs.

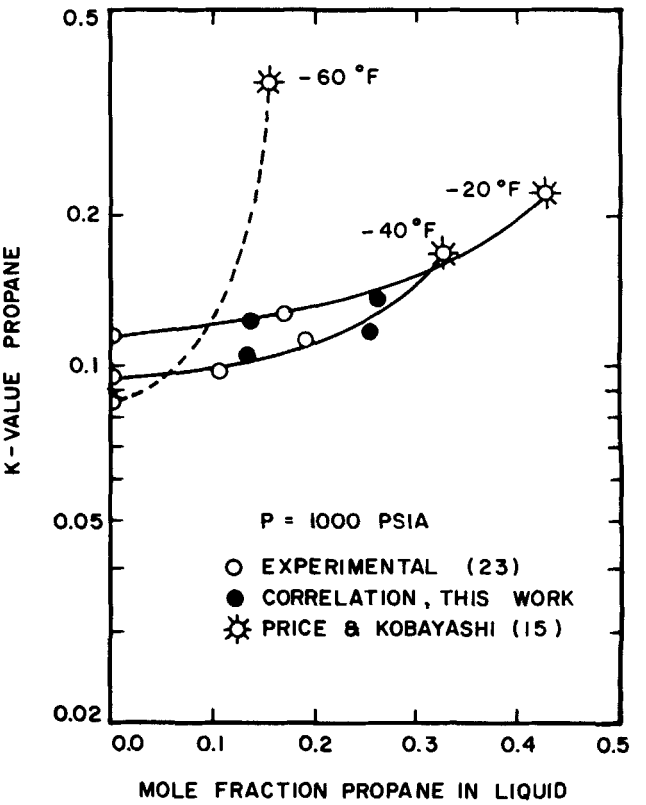

Fig. 7. Propane K value in the C_1–C_3–n-C_7 system. P = 1,000 lb./sq.in.abs.

Gas-liquid partition chromatography has proven to be a useful tool with which to determine K values. It is especially applicable to the determination of infinite dilution K values. The advent of GLPC makes determination of

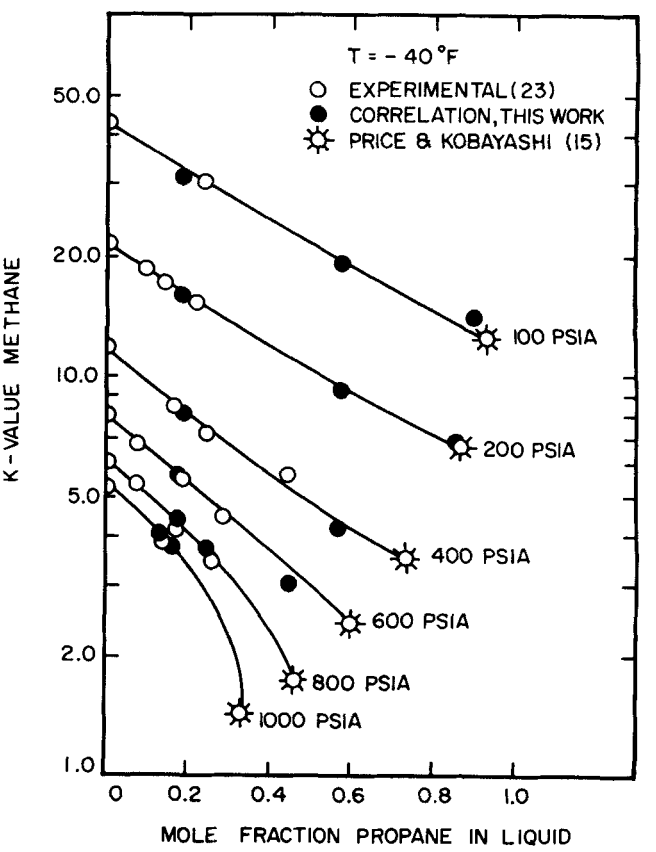

Fig. 8. Methane K value in the C_1–C_3–toluene system. T = —40°F.

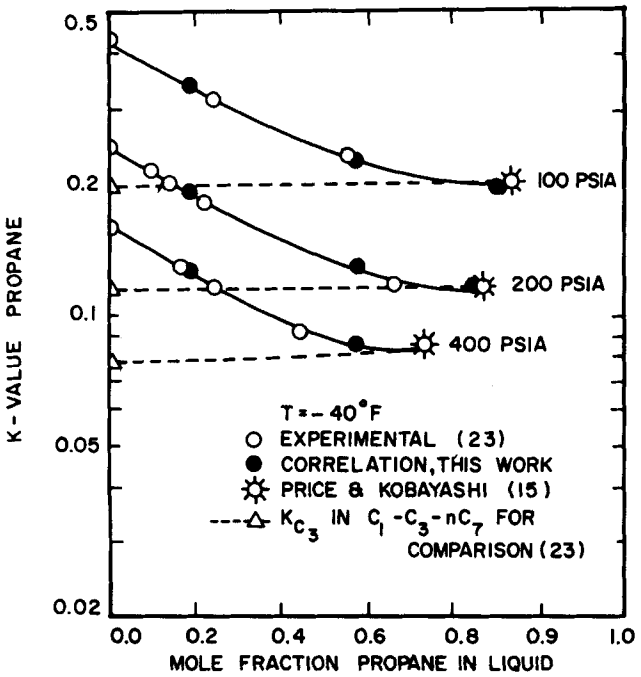

Fig. 9. Propane K value in the C_1–C_3–toluene system. Low pressure. $T = -40°F$.

infinite dilution K values for intermediate components in gas-heavy hydrocarbon systems feasible as a basis for further calculations. A considerable body of literature of infinite dilution K values for systems appropriate to this study is available (*22*, *9*, *23*). Accordingly, the infinite dilution K values of the intermediate components of the systems studied have been used in this work as basic data which are dependent only on pressure and temperature. Thus calculations were made to test a correlation of ethane and propane K values in the C_1-C_2-nC_7, C_1-C_3-nC_7, and C_1-C_3-toluene systems, reported in reference *23*, given the infinite dilution information.

The Scatchard-Hildebrand equation was rewritten as

$$\ln \gamma_i = \frac{E_i}{RT}(\delta_i - \delta_M)^2 \qquad (15)$$

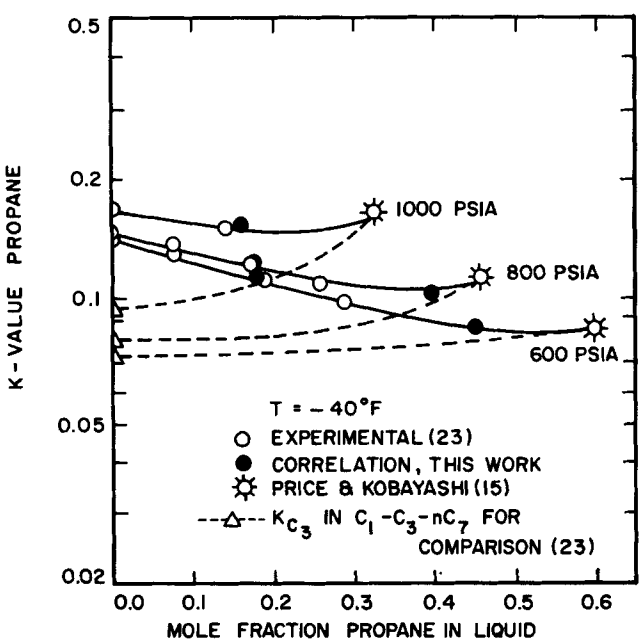

Fig. 10. Propane K value in the C_1–C_3–toluene system. High pressure. $T = -40°F$.

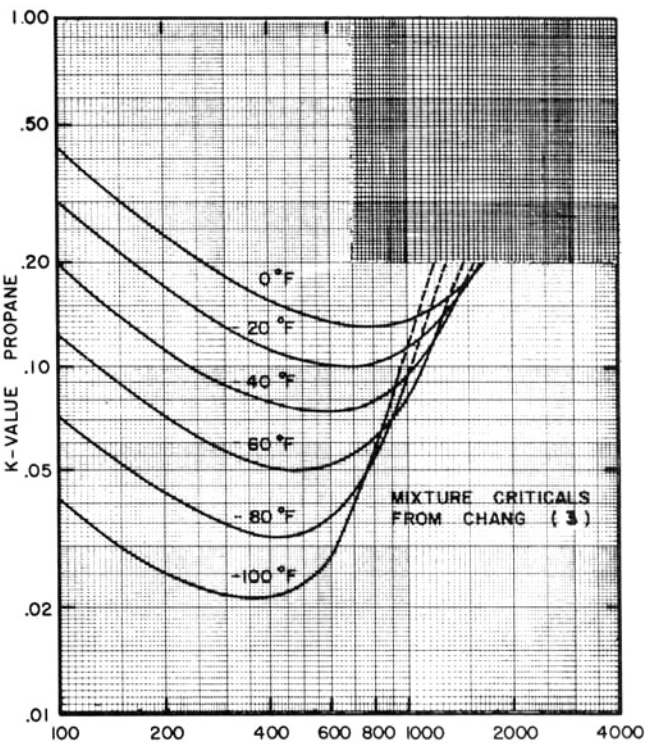

Fig. 11. K value for propane at infinite dilution in the C_1–n-C_7 system as function of pressure.

where E_i = an empirical parameter calculated from infinite dilution data.

$$\delta_M = \left(\sum_{i=1}^{N} x_i \delta_i V_i\right) \Big/ \left(\sum_{i=1}^{N} x_i V_i\right)$$

From Equations (1), (2), and (3)

$$K_i = \nu_i^{\circ} \gamma_i \left(\frac{y_i P}{f_i^V}\right) \qquad (16)$$

The pure component fugacity coefficients f_i° for ethane and propane were calculated from vapor pressures and PVT data. The B-W-R equation was used to evaluate the vapor

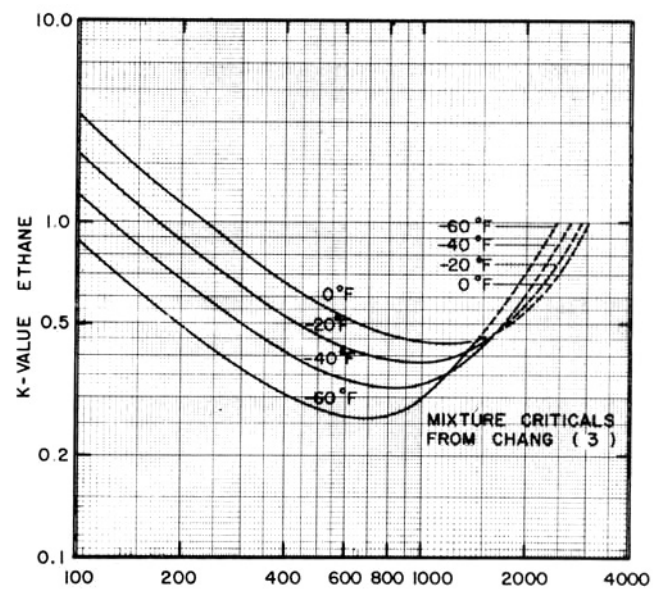

Fig. 12. K value for ethane at infinite dilution in the C_1–n-C_7 system as function of pressure.

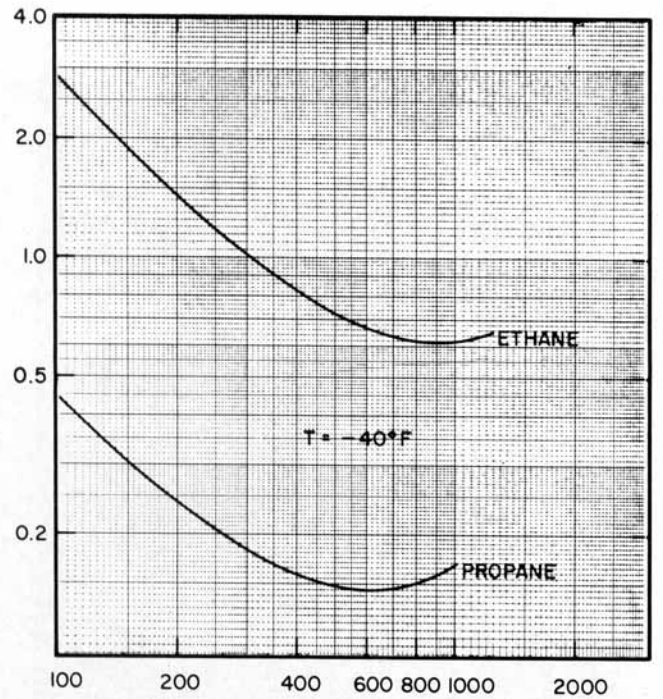

Fig. 13. *K* value for ethane and propane at infinite dilutions in the C_1–toluene system as function of pressure.

fugacity coefficients $[f_i^V/(y_iP)]$. γ_i, the liquid phase activity coefficient, was calculated from Equation (15) with E_i determined from the infinite dilution data in the following manner:

$$E_i = \frac{RT}{(\delta_i - \delta_M^\infty)^2} \ln [K_i^\infty [f_i^V/(y_iP)]^\infty/\nu_i^0] \qquad (17)$$

δ_M^∞ = liquid mixture solubility parameter evaluated from the liquid composition with component i at infinite dilution. For example, in the methane-propane-*n*-heptane ternary system, the liquid phase composition with propane infinitely dilute is the same as that of the methane-*n*-heptane binary system at the same temperature.

K_i^∞ = infinite dilution K value of the intermediate component i in the system. These K values are given in Figures 11 to 13 for ethane and propane in methane-*n*-heptane and methane-toluene.

$[f_i^V/(y_iP)]^\infty$ = vapor fugacity coefficient of i, calculated from the B-W-R equation for i at vanishingly small concentration in the vapor.

Once E_i was determined for a given set of conditions, Equations (15) and (16) were used to calculate K values of the intermediate component at finite concentrations in the system at the same temperature and pressure. In the ternary system methane-propane-*n*-heptane, for example, E_i was determined for propane, as discussed above, at the given temperature and pressure. Using this value of E_i, the K value of propane was calculated from Equations (15) and (16) for any propane composition in the ternary at the same temperature and pressure.

From the results of this work, it is proposed that similar but more complex, light hydrocarbon-hydrocarbon solvent systems can be predicted by using infinite dilution behavior of the intermediates in the binary formed by methane and the hydrocarbon solvent. Infinite dilution K values in binary systems are functions of temperature and pressure only for a given system as shown in Figures 11 to 13. The behavior of the binary systems which satisfy the restrictions of the methane correlation proposed in this paper can be satisfactorily calculated.

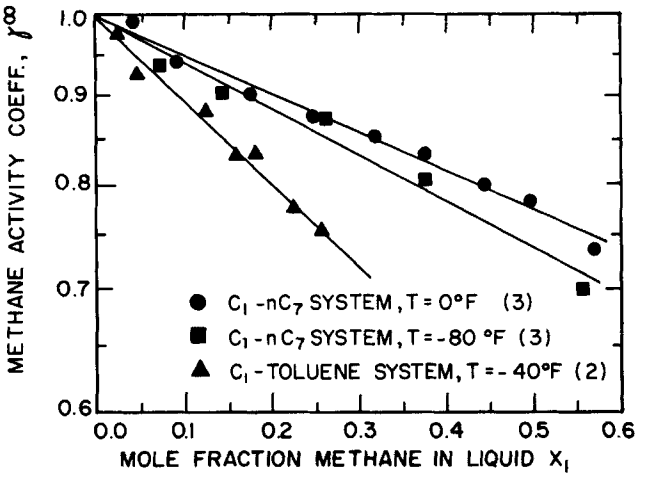

Fig. 14. Activity coefficient for methane based on infinite dilution standard state in C_1–*n*-C_7 and C_1–toluene.

This technique is tested here primarily for ternary systems. However, the technique did predict ethane K values for ethane at infinite dilution in the methane-propane-*n*-heptane and methane-propane-toluene ternary systems, as indicated in Table 4. This represents prediction of the behavior of an intermediate along a boundary of a quaternary system from its behavior at infinite dilution in a binary system.

The methane correlation and the correlations for ethane

TABLE 3. COMPARISON OF GENERAL METHANE CORRELATION WITH LITERATURE METHANE BINARY DATA

System	T, °F.	Positive No. of points	Positive error* Average percent	Negative No. of points	Negative error* Average percent
Methane–propane (15, 19)	50.0	5	5.9	3	−2.7
	40.0	3	3.1	4	−2.7
	0.0	1	5.7	5	−1.4
	− 50.0	1	0.9	3	−6.1
	−100.0	1	15.	2	−3.7
Methane–*n*-butane (17, 19)	100.0	5	1.8	0	
	40.0	2	6.1	14	−7.1
	− 20.0	0		11	−14.4
	− 80.0	2	9.1	3	−3.3
Methane–*n*-hexane (20)	32.0	0		8	−4.1
	− 13.0	0		8	−4.6
	− 58.0	0		8	−6.7
	−103.0	0		8	−5.1
Methane–*n*-heptane (3, 6, 16)	40.0	7	1.8	0	
	0.0	9	2.2	0	
	− 20.0	7	0.7	0	
	− 40.0	5	1.0	1	−0.7
	− 60.0	5	1.6	2	−1.5
	− 80.0	4	1.6	1	−0.6
	−100.0	3	2.4	0	
Methane–*n*-octane (7)	32.0	7	2.0	0	
	− 13.0	4	0.7	3	−0.2
	− 58.0	7	2.7	0	
Methane–*n*-nonane (21)	77.0	11	12.0	0	
	32.0	11	6.3	0	
	− 13.0	10	4.7	0	
	− 58.0	10	7.3	0	
Methane–*n*-decane (8, 19)	100.0	10	19.7	0	
	40.0	6	16.4	0	
	20.0	5	14.6	0	
	0.0	5	12.3	0	
	− 20.0	5	10.6	0	
Methane–toluene (2)	− 40.0	3	3.7	5	−3.2

$$*\text{Percent error} = \frac{K_{corr.} - K_{exp.}}{K_{exp.}} 100.$$

TABLE 4. COMPARISON OF PREDICTED AND EXPERIMENTAL K VALUES FOR METHANE, ETHANE, AND PROPANE IN TERNARY SYSTEMS

Component	System*	No. of Points	Avg. Abs. % Deviation	Temperature, °F.	Pressure, lb./sq. in. abs.
Methane	C_1-C_2-n-C_7	32	4.8	−20 to − 60	100 to 1,000
	C_1-C_3-n-C_7	42	4.5	−20 to −100	100 to 1,000
	C_1-C_3-Toluene	14	2.7	− 40	100 to 1,000
Ethane	C_1-C_2-n-C_7	32	1.9	−20 to − 60	100 to 1,000
	C_1-C_3-n-C_7†	37	1.7	−20 to − 60	100 to 1,000
	C_1-C_3-Toluene†	16	2.4	− 40	100 to 1,000
Propane	C_1-C_3-n-C_7	47	2.4	−20 to −100	100 to 1,000
	C_1-C_3-Toluene	16	2.4	− 40	100 to 1,000

*From reference *23*.
†Ethane at infinite dilution ($x_{C_2} = 0, y_{C_2} = 0$).

and propane were combined to provide a complete calculational scheme for methane, ethane, and propane K values in the systems studied. Heptane and toluene compositions in the vapor were assumed to be negligible. To ensure that the results would be internally consistent, the K values were calculated iteratively, with a flash calculation for new compositions between each iteration. Graphical examples of the results of these calculations are shown in Figures 4 to 10, for the methane-propane-n-heptane and methane-propane-toluene systems. Direct comparisons between experimental points and correlated points were made by fixing the vapor phase composition as that of the experimental point and then allowing the correlation to arrive at an iterated solution of K values and liquid compositions. The infinite dilution K values used in the computations are plotted in Figures 11, 12, and 13.

DISCUSSION

Comparisons between experimental data and predictions of the overall correlation are given in Tables 3 and 4. Table 3 compares experimental and predicted K values for methane in the binary systems studied. Table 4 is a comparison for methane, ethane, and propane K values in the ternary systems of reference *23*.

Reference to Table 3 shows the success of the general methane correlation in predicting methane K values in other binary systems through C_1-n-C_8. The predicted methane K values are somewhat better for methane in C_6 and higher molecular weight solvents (Table 1). As stated before, the correlation does not apply for methane liquid concentrations much greater than about 0.5 mole fraction.

The correlation for ethane and propane was based upon the Scatchard-Hildebrand equation. Strict use of the equation, as in the Chao-Seader correlation (*4*), was not satisfactory in paraffin systems. Proper behavior of the predicted K values in the selected systems was obtained by forcing the equation to predict the observed infinite dilution K values. The resulting K value predictions agreed very well with experimental results well into the ternary systems. Use of infinite dilution K values of the intermediate components in conjunction with the Scatchard-Hildebrand and B-W-R equations does provide for accurate prediction of the behavior of these components at finite concentrations in the multicomponent systems studied.

No reservations are made about the use of the Scatchard-Hildebrand equation for liquid activity coefficients in the aromatic system C_1-C_3-toluene. Direct use of the equation, using values for V_1, δ_1, and δ_2 estimated for −40°F., gave agreement within about 5% at infinite dilutions. The B-W-R equation can be used for the vapor, because toluene was essentially nonvolatile at the temperatures of this study, and thus the vapor was almost entirely methane and propane. Using the correlation method of this work, very close agreement was obtained with experimental results, even though compositional effects were quite large. This speaks well for the ability of the Scatchard-Hildebrand equation to predict the behavior of mixtures of paraffins and aromatics. It should be noted, however, that the tests for the mixtures of paraffins and aromatics are based on a smaller amount of data.

It was shown in this work that a correlation using the Scatchard-Hildebrand equation to describe liquid behavior and the B-W-R equation for vapor behavior gave excellent results predicting K values of the lower molecular weight hydrocarbons in paraffin and aromatic systems, when used in conjunction with experimental infinite dilution K value data. It is felt that this procedure has general application as well, because it combines the proven generality and qualitative features of the Scatchard-Hildebrand equation (*4*) with the guarantee of obtaining the quantitative accuracy desired through the incorporation of experimental infinite dilution data in the calculations.

ACKNOWLEDGMENT

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NOTATION

A, B, C, D = empirical constants
ΔE = isothermal molar change in energy in going from liquid to gas
f^L = partial fugacity in the liquid
f^V = partial fugacity in the vapor
K = vapor-liquid equilibrium constant, y/x
n = number of carbon atoms in the molecule
P = total system pressure
P_C = critical pressure
P_o = reference pressure where solute as at infinite dilution; taken as 1 atm.
R = gas constant
T = absolute temperature
T_C = critical temperature
V = molar volume
$\overline{V}$ = partial molar volume
x = mole fraction in the liquid phase
x' = mole fraction in the liquid, corrected to a methane-free basis
y = mole fraction in the vapor phase

Greek Letters

δ = solubility parameter = $\left(\frac{\Delta E}{V}\right)^{1/2}$

γ = activity coefficient

ϕ = volume fraction of component in the liquid = $\frac{x_i V_i}{\Sigma x_i V_i}$

ν^o = fugacity coefficient of pure component at the T, P of the system

Subscripts

1 = light component
2 = solvent
i = general pure component

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Laminar Dispersion in Capillaries: Part V.

Experiments on Combined Natural and Forced Convection in Vertical Tubes

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An approximate theory for transient dispersion with combined free and forced convection in vertical tubes is developed and tested experimentally. It is found that the dispersion coefficient in such systems depends on a parameter α, which is defined by Equation (38). The analytical expression developed for the dispersion coefficient, Equation (33), is found to be a reasonably good approximation in the range $-50 < \alpha < 300$.

Experimental results are reported for a rather wide range of parameters for tubes with both 1½ and 5 mm. diameters.

It is found that the extent of dispersion is enhanced significantly when lighter fluid is on the bottom and displaces a heavier one. On the other hand, the dispersion coefficient is inhibited when the situation is reversed. It is found that these effects are not symmetrical with respect to the absolute magnitude of the parameter α as is illustrated in Figure 12.

Work on dispersion in tubes (*1* to *8*, *11* to *13*, *15* to *17*) has produced a very clear picture of this phenomenon in cases where natural convection effects are negligible. It remains to study the effects of density differences on dispersion in tubes and eventually to apply this new knowledge to porous media. In a previous report (*1*) it was indicated from the data on horizontal tubes that natural convection can both depress and accentuate the observed dispersion coefficient substantially as compared with that predicted by laminar flow theory which neglects natural convection effects. One would expect natural convection to play a substantially more important role in dispersion in vertical systems and therefore this process is studied here. In this discussion all flows are isothermal and density differences are caused solely by concentration differences.

The exact mathematical solution of the transient convective diffusion equation with natural convection effects is very difficult to obtain since the velocity profile will be distorted from the normal parabolic shape. Hence the unsteady momentum and diffusion equations must be solved simultaneously in order to describe the dispersion process. However, the analysis of the vertical tube is simpler compared with that of the horizontal tube because of the symmetry with respect to gravity.

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