The Correlation of Vapor-Liquid Equilibria of Methane in Paraffinic, Naphthenic, and Aromatic Solvents at Low Temperatures and High Pressures

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Several different approaches, such as the convergence pressure concept, equations of state, the application of the principle of corresponding states, etc., have been tried for the correlation of vapor-liquid equilibria of hydrocarbons for many years. The NGAA Data Book (*30*) is an example of the application of the convergence pressure concept which was originated by Organick and Brown (*32*) and later developed by Hadden (*14*). The well-known eight-parameter Benedict-Webb-Rubin (BWR) equation of state (*2*) and the simple two-parameter Redlich-Kwong (R-K) equation of state (*37*) have been used to some extent. Leland and co-workers (*22* to *25*) have developed a method to predict vapor-liquid equilibria based on the corresponding states principle. A method of correlation with the solubility parameter concept and certain aspects of the corresponding states theory was given by Chao and Seader (*8*). The applicability of each method of correlation is restricted to certain systems and limited temperature and pressure conditions. The purpose of this paper is to present a method to predict the phase behavior in binary systems containing methane and a relatively heavy component which can be paraffinic, naphthenic, or aromatic, such as *n*-heptane, methylcyclohexane, or toluene. Temperatures of interest in this correlation range from 330° to 500°R. and pressures from 100 to several thousand lb./sq.in.abs. The highest pressure data used were at 3,822 lb./sq.in.abs. and 492°R. for the methane-*n*-nonane system. Extension of the general approach to multicomponent systems is underway.

The method of correlating vapor-liquid equilibria data in this work is based on the separation of the deviations of the *K* value from ideality into deviations occurring in the vapor phase and liquid phase separately; these deviations are then correlated with thermodynamically consistent expressions. In this method, the vapor phase nonideality is calculated from the modified R-K equation of state (*44*, *45*); the liquid nonideality is calculated with reference to the pure liquid components and the deviations from ideal solution laws.

DESCRIPTION OF THE CORRELATION

The vapor-liquid equilibrium constant K_i of component *i* in a binary mixture may be derived from the rigorously defined thermodynamic quantities

$$f_i^V = \phi_i \, y_i \, P \tag{1}$$

$$f_i^L = \gamma_i \, x_i \, f_i^o \tag{2}$$

The temperature ranges in this work are such that

$$T > T_{c,1} \tag{3}$$

$$T < T_{c,2} \tag{4}$$

At equilibrium

$$f_i^V = f_i^L \tag{5}$$

Thus

$$\phi_i \, y_i \, P = \gamma_i \, x_i \, f_i^o \tag{6}$$

and

$$\frac{y_i}{x_i} = (f_i^o/P)\,(\gamma_i/\phi_i) \tag{7}$$

By definition, the equilibrium constant K_i is the ratio of the mole fraction of component *i* in the vapor phase to the mole fraction of component *i* in the liquid phase. Thus

$$K_i = y_i/x_i = (f_i^o/P)\,(\gamma_i/\phi_i) \tag{8}$$

Fugacity Coefficient of Pure Liquid Components

Pitzer's modified form of the principle of corresponding states gives the expression as

$$\log\,(f_i^o/P) = \log\,(f_i/P)^o + \omega \log\,(f_i/P)^1 \tag{9}$$

The quantities $(f_i/P)^o$ and $(f_i/P)^1$ depend only on the reduced temperatures and reduced pressures. They have been closely fitted with empirical functions by Chao and Seader (*8*).

Fugacity Coefficient in the Vapor Phase

These quantities may be obtained from an equation of state such as the BWR or the R-K. Since the eight-parameter BWR equation of state is more complicated and more labor will be involved to obtain ϕ_i, the simpler two-parameter R-K equation of state was modified (*45*) and chosen in this calculation.

The original R-K equation (*37*) may be rearranged to give

$$\frac{PV}{RT} = \left(\frac{V}{V-b}\right) - \left(\frac{a}{bkT^{1.5}}\right)\left(\frac{b}{b+V}\right) \tag{10}$$

The modified temperature-dependent parameter in the R-K equation was developed by Wilson (*44*) by assuming that

$$a/(bRT^{1.5}) = F(T_c/T, \omega) = D_1 + D_2/T \tag{11}$$

Then the following relation was obtained:

$$F(T_c/T, \omega) = 4.934\,[1 + (1.45 + 1.62\omega)\,(T_c/T - 1.0)]\;(T_c/T)^{0.12} \tag{12}$$

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Combining Equations (11) and (12), rearranging, and applying to component i, one obtains

$$a_i = F(T_{ci}/T, \omega)\, b_i R T^{1.5} \tag{13}$$

and

$$A_i^2 = a_i/(R^2\, T^{2.5}) \tag{14}$$

$$A = \sum_i y_i\, A_i \tag{15}$$

$$B_i = 0.0867\;\, T_{ci}/(P_{ci}\, T) = 0.0867/(P_{ci}\, T_{ri}) \tag{16}$$

$$B = \sum_i x_i\, B_i \tag{17}$$

$$b_i = 0.0867\;\, R\;\, T_{ci}/P_{ci} \tag{18}$$

Then the vapor phase fugacity coefficient may be evaluated through

$$Z = \left(\frac{1}{1-h}\right) - \frac{A^2}{B}\left(\frac{h}{1+h}\right) \tag{19}$$

$$h = BP/Z \tag{20}$$

$$\log \phi_i = 0.4343(Z - 1.0)(B_i/B) - \log(Z - BP) - (A^2/B)(2A_i/A - B_i/B)\log(1 + BP/Z) \tag{21}$$

The compressibility factor Z of the vapor mixture was calculated by trial and error from Equations (19) and (20).

Activity Coefficient in the Liquid Phase

The activity coefficient γ_i is usually expressed in either the van Laar or the Margules type of equation. Hildebrand's equation, which belongs to the van Laar type and is based on the regular solution theory (*17*), has been used by many investigators in the correlation of vapor-liquid equilibria and has given very successful results for many systems at certain conditions. But it fails to predict the equilibrium ratio for molecules of large size differences, such as the mixtures of methane-*n*-nonane and methane-*n*-decane. As early as 1938, Sage and Lacey (*39*) noted that for a fixed pressure and temperature, the methane K value increases with the carbon number of solvents up to a certain maximum point and then decreases slightly. Van Horn (*43*) plotted methane K values in various paraffinic solvents at 0°C. and 10 atm. pressure with the carbon number of the solvent and found the maximum to occur around *n*-nonane. It is not surprising that Hildebrand's equation cannot predict this unusual behavior because the Hildebrand regular solution theory is applicable mainly to the solution of nonpolar or slightly polar molecules of equal size that form a positive enthalpy of mixing. These solutions possess a zero excess entropy term (ideal entropy of mixing) and contain a random distribution of molecules (no orientational or associative effects).

The thermodynamic properties of solutions of molecules of different size may be discussed in terms of a Miller-Guggenheim (*12, 29*) or Flory-Huggins (*9, 18*) theory. The structure of the mixture is defined by z (the number of sites that are nearest neighbors to a given segment of molecule on the quasi crystalline lattice) and by r (the size ratio of the two molecules), and the energies of interaction between like and unlike molecules are expressed by an energy parameter χ. The consistency and utility of combining the Hildebrand and MG-FH theories for mixtures of molecules of unequal size have been successfully demonstrated recently (*3, 15, 16, 27*). This correlation follows the approach of these combined theories, except that the energy parameter χ is used instead of the solubility parameter in the Hildebrand equation.

Ashworth and Everett suggested (*1*) that to a first approximation the deviations from Raoult's law exhibited by solutions of molecules differing in size may be expressed as the sum of two contributions to the logarithm of the activity coefficients

$$\ln \gamma_i = \ln \gamma^{ath} + \ln \gamma^{th} \tag{22}$$

where γ^{ath} arises solely from statistical effects related to the difference in size of the molecules and is independent of temperature, and γ^{th} is a temperature dependent term associated with the interaction energies between the various molecular species present. For small values of $\ln \gamma^{th}$, the γ^{th} and γ^{ath} are approximately independent of one another, but if large energy effects exist, the statistical term is modified because of the higher weighting which must be attached to configurations of lower energy (higher energy of interaction).

The form of $\ln \gamma^{ath}$ was given by Miller-Guggenheim as

$$\ln \gamma_1{}^{ath} = \ln[(1 - \psi_2)/x_1] - z/2 \ln[1 - (1 - 1/r_1)2\psi_2/z] \tag{23}$$

where

$$\psi_2 = \frac{r_1\; x_2}{x_1 + r_1\; x_2} \tag{24}$$

The form of $\ln \gamma^{th}$ has not been established theoretically with any certainty. The expression

$$\ln \gamma^{th} = \chi\; \psi_2{}^n \tag{25}$$

is used in this work, where χ and n are fitted by the experimental data of eight binary hydrocarbon systems (methane-*n*-butane to methane-*n*-decane, methane-toluene, and methane-methylcyclohexane).

In accordance with the simple form of solution theory, χ is related to the so-called *interchange energy* E by the equation

$$\chi = (zE)/(kT) \tag{26}$$

The number of nearest neighbor sites z was chosen as twelve, since most common lattices have a coordination number about this value. Equation (23) shows that γ^{ath} is highly insensitive to the choice of a value of z when z is large. The interchange energy E was given by Ashworth and Everett (*1*) as

$$E = \tfrac{1}{2}\,(E_{11} + E_{22}) - E_{12} \tag{27}$$

The energy parameter E itself is slightly temperature dependent. But E may be treated as a constant if the temperature range under consideration is not excessively wide. For the temperature range of this study, 40° to −130°F., E is a constant.

Empirical Development of the Energy Parameter χ

From Equation (8) one obtains

$$\ln \gamma_i = \ln\,(\phi_i\; K_i) - \ln\,(f_i{}^o/P) \tag{28}$$

Substituting Equations (22) and (25) into Equation (28) and rearranging, one obtains

$$\chi = [\ln(K_i\phi_i) - \ln\,(f_i{}^o/P) - \ln \gamma_i{}^{ath}]\; \psi^{-n} \tag{29}$$

In Equation (29), all the functions in the right-hand side may be obtained from the previous sections and K_i from the experimental data. At each isotherm χ may be calculated by a data fitting process. It has been found that $n = 2.6$ gives the best results. The interchange energy E may then be computed by Equation (26). Conversely, whenever the energy parameter χ is known, K values are computed by the combination of Equations (25), (23), (21), and (9).

PRESENTATION AND DISCUSSION OF THEORETICAL RESULTS

TABLE 1. COMPARISON OF THE AVERAGE PERCENT DEVIATION FOR METHANE K VALUE BY CORRELATION IN EIGHT BINARY SYSTEMS

System	Temp. range, °*R.*	No. of positive pt.	Avg. dev., %	No. of negative pt.	Avg. dev., %
Methane-*n*-butane	380 to 440	6	2.492	7	— 3.821
Methane-*n*-hexane	330 to 402	9	2.682	5	— 1.540
Methane-*n*-heptane[*]	330 to 460	20	2.177	5	— 1.566
Methane-*n*-heptane	360 to 460	25	1.712	35	— 3.545
Methane-*n*-octane	402 to 492	5	2.448	5	— 1.278
Methane-*n*-nonane	402 to 492	16	1.536	13	— 1.545
Methane-*n*-decane	440 to 500	12	0.895	8	— 1.080
Methane-methylcyclohexane	360 to 460	37	2.491	40	— 2.759
Methane-toluene	360 to 460	45	3.26	26	— 1.650

% dev. = $[(K_{\text{exp}} - K_{\text{cal}})/K_{\text{exp}}] \times 100$

[*] Data of Kohn (*19*).

The average relative deviation of the calculated K values for methane for the eight binary systems and the three C-7 systems is presented in Table 1. These include binary systems of methane-*n*-paraffin (from methane-*n*-butane to methane-*n*-decane), methane-methylcyclohexane, and methane-toluene. Table 2 presents the temperature and pressure ranges to which the correlation has been applied, and Table 3 gives some physical properties of the hydrocarbons.

TABLE 2. PRESSURE AND TEMPERATURE RANGES FOR SOME RELATED METHANE-*n*-PARAFFIN SYSTEMS USED IN THE STUDY

Systems	T, °*R.*	Pressure range, lb./sq. in. abs.	Reference
C_1-n-C_4	440	120.0 to 1645.0	*38*
	380	110.0 to 975.0	*38*
C_1-n-C_6	402	147.0 to 1176.0	*40*
	357	73.5 to 882.0	*40*
	330	294.0 to 514.5	*40*
C_1-n-C_7	460	200.0 to 1500.0	*19*
	420	200.0 to 1500.0	*19*
	380	200.0 to 1000.0	*19*
	360	100.0 to 800.0	*19*
	340	200.0 to 600.0	*19*
	330	200.0 to 500.0	*19*
C_1-n-C_8	492	147.0 to 1029.9	*20*
	402	147.0 to 1029.0	*20*
C_1-n-C_9	492	147.0 to 3822.0	*41*
	447	147.0 to 1470.0	*41*
	402	294.0 to 1470.0	*41*
C_1-n-C_{10}	500	251.5 to 925.5	*21*
	480	227.2 to 969.8	*21*
	460	227.0 to 916.5	*21*
	440	232.0 to 1000.7	*21*

TABLE 3. SOME PHYSICAL PROPERTIES AND PARAMETERS OF THE PURE HYDROCARBONS

Component	T_c, °*R.*	P_c, lb./sq. in. abs.	ω	δ	V	χ, 420°*R.*	*m.p.*,°*R.*
Methane	343.7	673.26	0	5.68	52.0		163.5
n-butane	766.0	549.78	0.1953	6.73	101.4	0.545	243.1
n-hexane	915.0	432.18	0.2927	7.27	131.6	0.840	320.5
n-heptane	972.5	393.96	0.3403	7.43	147.5	0.885	328.9
n-octane	1,025.0	361.62	0.3992	7.55	163.5	0.996	389.7
n-nonane	1,072.0	338.10	0.4439	7.65	179.6	1.050	395.5
n-decane	1,114.0	323.40	0.4869	7.72	196.0	1.090	438.5
Toluene	1,069.1	611.52	0.2591	8.92	106.8	1.600	321.0
Methylcyclohexane	1,035.0	588.00	0.2421	7.83	128.3	1.155	264.4

ω = acentric factor
δ = solubility parameter
V = molar volume, cc./mole
χ = interchange energy parameter between methane and solvent-type hydrocarbon

Two data sources for the methane-*n*-heptane systems have been used in this computation. The agreement of calculated values for both sets of data is very good. Plots of the experimental (*5* to *7*) calculated *K* values for methane-*n*-heptane, methane-methylcyclohexane, and methane-toluene systems at —40°F. are presented in Figures 1, 2, and 3. The experimental data are internally consistent, but the absolute *K* value of the heavy component is uncertain.

We have also made a comparison of the Chao-Seader correlation results with the experimental data (*4*). The deviation is shown to be less than 50% in most cases.

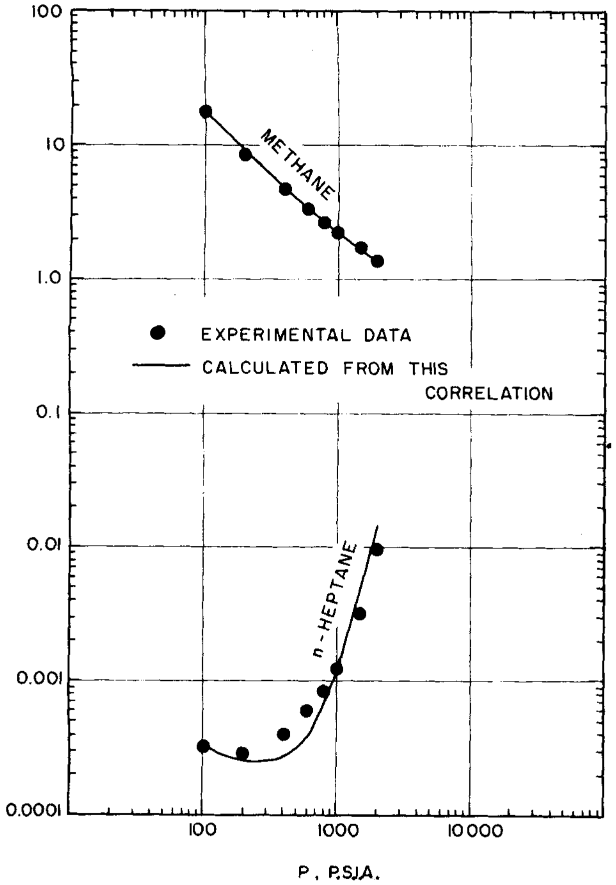

Fig. 1. Comparison of the experimental (5) and calculated *K* values in the methane-*n*-heptane system at —40°F.

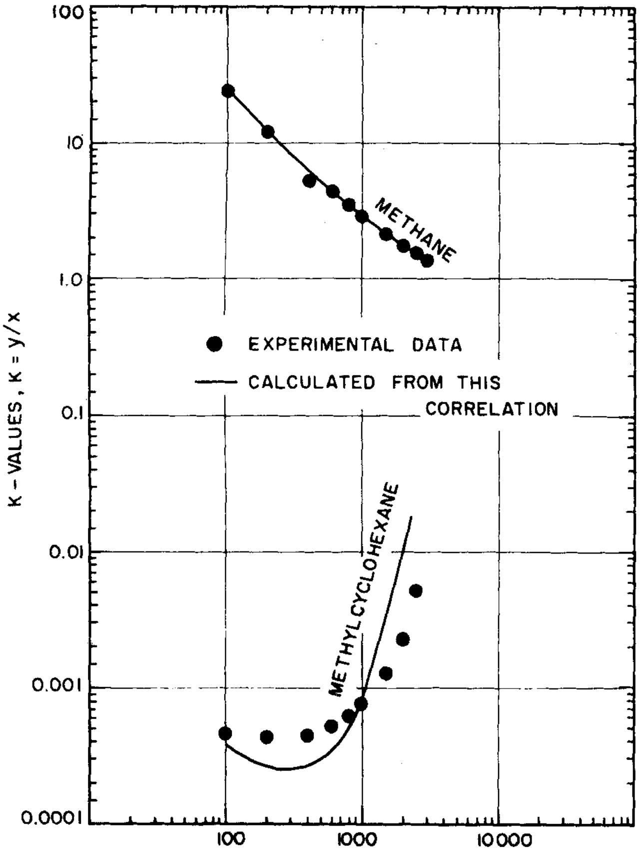

Fig. 2. Comparison of the experimental (6) and calculated *K* values in the methane-methylcyclohexane system at —40°F.

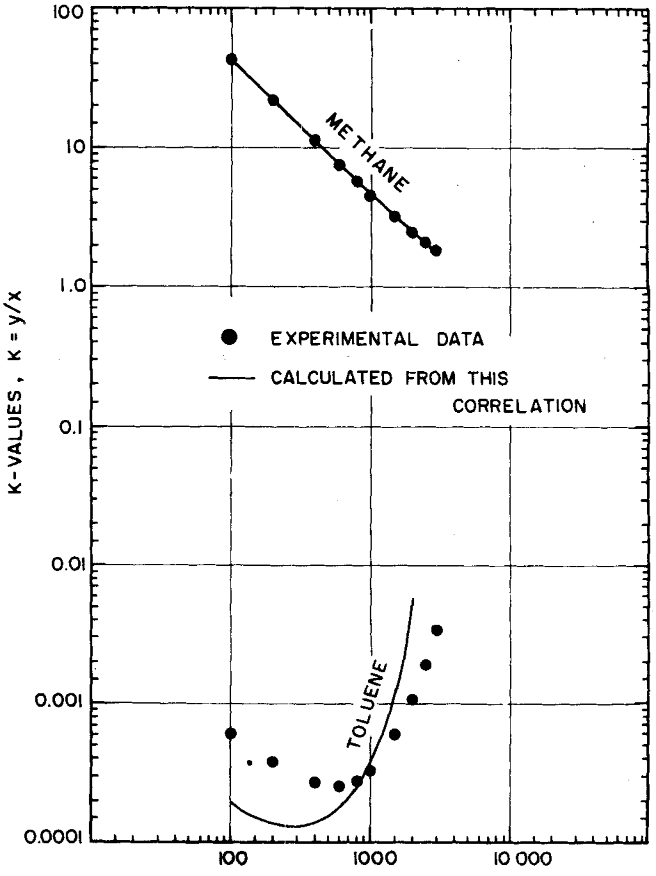

Fig. 3. Comparison of the experimental (7) and calculated *K* values in the methane-toluene system at —40°F.

K Values for Methane

The computational results are in good agreement for the methane K values except near the critical point. The deviations are less than 5% for 90% of the calculated points. Generally, methane K values may be predicted with the deviation falling within ± 5% of the experimental data up to 0.70 mole fraction of methane in the liquid phase; in some cases, the prediction is good even up to 0.80 mole fraction of methane in the liquid phase. The failure in predicting the K value near the critical region is due to the sharp increase of the concentration of methane in the liquid phase.

K Values for the Heavy Components

Only three binary systems (methane-*n*-heptane, methane-methylcyclohexane, and methane-toluene) have been used in the theoretical study because data are not available on other systems at such low temperatures to −100°F. The detailed comparison of the experimental and calculated K values for *n*-heptane, methylcyclohexane, and toluene has been made elsewhere (*4*). The average relative deviation for the heavy component K values ranged from +20 to −200%. The deviations increased as the temperature decreased and were in the order toluene>methylcyclohexane>*n*-heptane. The comparison shows that the application of the correlation to the solvents is not nearly as successful as to methane, especially at high pressures. The comparison of the results by this correlation with the original Chao-Seader correlation shows that the deviation from the experimental data falls into the same order of magnitude. This failure is caused by the unsuccessful prediction of the nonideality of the heavy component in the vapor phase by the equation of state (R-K). To the authors' knowledge, there are no other equations which would predict the vapor phase nonideality for such heavy components at such low temperatures.

Relative Importance of Each Term in the Correlation

Liquid Fugacity Coefficient of the Pure Component For the Solvent-Type Heavy Components. The fugacity coefficient of the pure liquid (f_i^o/P) is a thermodynamically well-defined property for the heavy hydrocarbons. It may be considered as the ideal K value for the individual component. A correlation based on Pitzer's corresponding states principle has been developed by Chao and Seader (*8*) which was used in this work. The application of this correlation to low temperatures is not as successful as to high temperatures. A better correlation might be achieved if low temperature vapor pressure data were available.

Liquid Fugacity Coefficient of the Pure Component For Methane. Since the temperature range studied here is above the critical temperature of methane, a hypothetical pure liquid standard state at the temperature of the solution is used. Temperature and pressure together with the critical properties were used to specify the properties of the hypothetical liquid. A special set of constants (*8*) with $\omega = 0$ was used in Equation (9) to compute the fugacity coefficient of the hypothetical liquid methane. The concept of the hypothetical standard state has been discussed elsewhere (*26*).

Another way for defining the reference fugacity of light components, as proposed by Prausnitz (*35*) and Orentlicher and Prausnitz (*31*), is based on the infinite dilution approach. They have applied this method to study the solubility of hydrogen in cryogenic solvents at high pressures. This technique has also been applied to correlate the K values in methane-hydrocarbon systems by Van Horn (*43*). The advantage of using the infinite dilution approach for reference fugacity is that it is, being derived from real rather than imaginary physical data, unambiguously defined. Hence, for a given situation there is a definite numerical value. The disadvantage of this reference fugacity is that it not only depends on the properties of the liquid component but also depends strongly on the properties of the heavy component; therefore, this reference fugacity for methane is also a function of the solvent, such as *n*-heptane, methylcyclohexane, or toluene in the systems under study. However, in the hypothetical standard state approach the effect of solvent properties must appear in the activity coefficient of the liquid phase.

Vapor Phase Fugacity Coefficient ϕ_i For Methane. The fugacity coefficient for methane in the vapor phase is close to unity when the pressure is low. As the pressure is increased, it decreases only slightly. This is because the vapor phase contains mostly methane at low temperature and all pressures. For the methane-*n*-heptane system, dew point data at low temperatures show that all vapor phases at temperatures below 0°F. contained less than 0.001 mole fraction *n*-heptane at all pressures higher than 100 lb./sq.in.abs. except near the critical region. Therefore, the simple two-parameter R-K equation of state did give very satisfactory results in the correlation for vapor phase fugacity coefficient for methane.

Vapor Phase Fugacity Coefficient ϕ_i For Heavy Components. The vapor phase fugacity coefficients for the heavy components are also close to unity at low pressures. As the pressure is increased, they decrease markedly. For example, for *n*-heptane $\phi = 0.802$ at 0°F. 100 lb./sq.in. abs., but it decreases to 0.004 at 2,500 lb./sq.in.abs. at the same temperature. This sharp decrease indicates the importance of the nonideality which exists in the vapor phase for heavy components. As the temperature decreases, this behavior becomes more serious. This is the chief cause for the failure in predicting the K values for the heavy components. A further modification for the equation of state would be the inclusion of the effect of the intermolecular forces acting between unlike molecules on the mixing rule which relates the constants of a mixture to those of the pure components.

Prausnitz (*34*) suggested that ϕ_i may be computed by the virial coefficient technique which was derived from the statistical mechanics (*10, 11*). An exact expression for the fugacity coefficient of component i in the gas mixture has been given as

$$\ln \phi_i = 2\rho \sum_{j}^{n} y_j\, B_{ij} + \frac{3}{2}\rho^2 \sum_{j}^{n}\sum_{k}^{n} y_j\, y_k\, C_{ijk} - \ln Z \tag{30}$$

The compressibility factor may be expressed as

$$Z = PV/(RT) = 1 + B\rho + C\rho^2 + D\rho^3 + \ldots \tag{31}$$

The above equations are difficult to use owing to the lack of density and virial coefficient data for the mixtures. Fortunately, the fugacity coefficient is much more sensitive to the second virial coefficient than to the third virial coefficient. In many cases, it is permissible to neglect the third virial coefficients entirely. Methods of estimating the virial coefficients for simple gas mixtures have been proposed by Guggenheim and McGlashan (*13*), Prausnitz and Gunn (*36*), and Prausnitz (*34*). This approach seems promising for computing the low density vapor phase fugacity if the necessary data are available or estimative.

The Liquid Phase Activity Coefficient. The activity coefficient in the liquid solution approaches unity for the component present in high concentration in the liquid phase. It reflects the nature of the solvent such as aromaticity and size.

The difference in the molecular sizes is one of the important factors in the liquid phase nonideality. Since the size ratio is large, the Miller-Guggenheim expression for the *ath* activity coefficient is adopted in this calculation. This term is given in Equation (23) and is temperature independent. The temperature dependent part *th* activity coefficient which reflects mainly the enthalpy of mixing is taken from Flory-Huggins (*9, 18*) formulation with the modification of the volume fraction index.

Two terms in Equations (23) and (24) have particular interest.

1. The size ratio r: It is difficult to arrive at a rational method for defining r in terms of molecular structure in most cases; therefore, the empirical procedure of defining r as the ratio of the molar volumes of the pure liquids at the temperature of experiment is necessary. However, owing to the difficulty in obtaining low temperature volumetric data for the systems studied, r is taken as the volume ratio at 25°C., since the ratio is quite insensitive to temperature at low temperatures. As a result, the simple theoretical interpretation of r in terms of segments of molecules is obscured. For large temperature ranges, however, r should still be considered a function of temperature; then ln γ^{ath} will also be a function of temperature and therefore contribute a configurational term to the heat of mixing.

2. The energy parameter χ: This term is related to the so-called *interchange energy E* by Equation (26). From the computation of eight hydrocarbon systems, it has been found that, with solvents of the same carbon number, the interchange energy of the methane-aromatic system is higher than that of the methane-napthene system which is higher than that of the methane-*n*-paraffin system. This explains the high K value of methane in aromatics or naphthenics and accounts for the aromaticity correction factor in common use for the light components (*42*). Among the methane-*n*-paraffin systems the interchange energy increases rapidly with the carbon number of the solvent starting from methane-ethane but begins to level off for the mixtures with solvents heavier than *n*-hexane, as indicated in Figure 5.

From Equation (27) one may conclude that the large value of E may arise from an abnormally large value of either E_{11} or E_{22} interactions. This work confirms earlier observations (33) that mixtures of aromatic and aliphatic substances have a large value of E, while aliphatic-aliphatic or aromatic-aromatic systems have a small value of E. Although it seems too soon to identify the particular interaction energy to which these large values of E are to be attributed, there is some evidence (33) that weak aromatic-aliphatic interactions play a dominating role. Therefore, the energy parameter χ has to depend on the nature of the solute and solvent but not appreciably on the molecular weight as long as the molecular weight of the solvent is high. There are evidences (*27, 28*) that this should be so for high molecular weight paraffin solvents. This seems to suggest that the interaction parameter should approach a limiting value where the solvent end effects become less important.

Overall, it is found that, qualitatively, the interaction parameter falls into the same order as the heats of evaporation, although the variation is not in exact agreement with the Hildebrand-Scatchard treatment of the heats of mixing (*17*). A plot of χ vs. the solvent carbon number is given in Figure 4. A plot of χT vs. carbon number which combines the isotherms of Figure 4 into a single line is given in Figure 5.

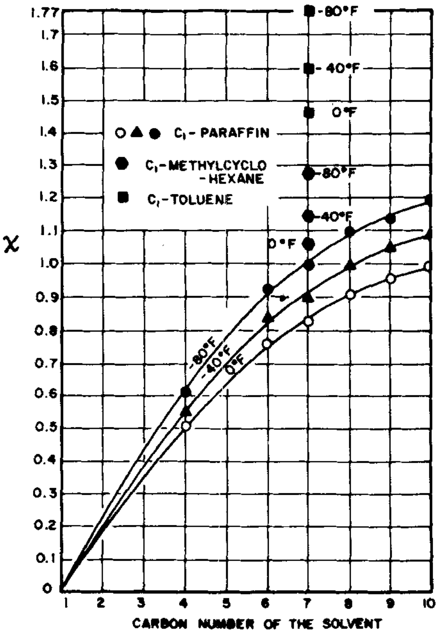

Fig. 4. Energy parameter vs. carbon number of the solvent.

A study of Figure 5 suggests that it may be possible to predict behavior over a temperature range from a few measurements at only one temperature. Similarly, one can imagine other homologous series which would include the present isolated naphthenic and aromatic points. It would be useful to know the full extent of the temperature range for which the χT correlation holds; the range covered here is given in Table 2.

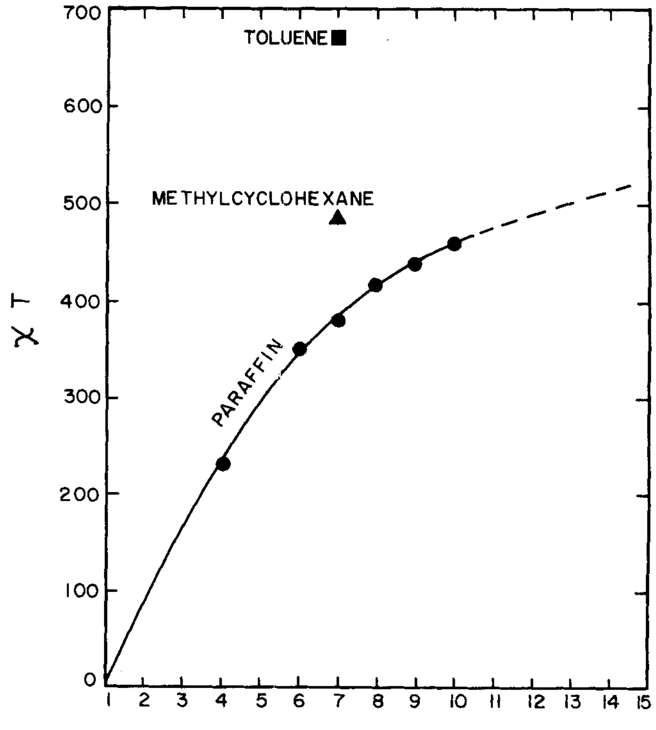

Fig. 5. Temperature independent correlation.

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NOTATION

A = parameter in the Redlich-Kwong equation of state
a = parameter in the Redlich-Kwong equation of state
B = parameter in the Redlich-Kwong equation of state
b = parameter in the Redlich-Kwong equation of state
B, C = virial coefficient
D_1, D_2 = constants
E = interchange energy
F = modified temperature-dependent parameter in the Redlich-Kwong equation of state
f = fugacity
h = arbitrary function in the Redlich-Kwong equation of state
K = vapor-liquid equilibrium constant
k = Boltzmann constant
n = empirical constant Equations (25) and (29)
P = total pressure
P^o = vapor pressure
R = gas constant
r = molecular size ratio at 25°C.
T = temperature
V = molar volume
x = mole fraction in the liquid phase
y = mole fraction in the vapor phase
Z = compressibility factor
z = number of nearest neighbor sites to a given segment of a molecule

Greek Letters

ω = acentric factor
γ = activity coefficient in the liquid phase
χ = energy parameter
ρ = density
ϕ = vapor phase fugacity coefficient
ψ = volume fraction
Σ = summation

Superscripts

ath = athermal
L = liquid phase
$^\circ$ = reference state
th = thermal
V = vapor phase

Subscripts

i, j, k = component identification
$1, 2$ = methane and solvent component identification
c = critical identification
r = reduced property identification
s = standard state

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