Computation of Vapor Liquid Equilibria for Hydrogen and Light Hydrocarbon Systems

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Generalized expressions are presented for Henry's constants and self-interaction constants required in the Chueh-Prausnitz method for predicting the vapor-liquid equilibria for hydrogen and light hydrocarbon systems. The *K*-values calculated using the above correlations were compared with the *K*-values obtained from the published experimental data in the temperature range of 117 to 422°K. The statistical analysis shows that the calculated values are about as reliable as the experimental results.

SCOPE

In the petrochemical industry high purity light olefins are produced by fractionation of light hydrocarbon mixtures. For proper design of the fractionation systems a reliable method for the prediction of vapor liquid equilibria is required. The prediction of vapor liquid equilibria for the light hydrocarbon mixtures is complicated mainly because hydrogen and methane exhibit abnormal thermodynamic behavior. Moreover, in many cases the components are present in the liquid phase at temperatures above their critical temperatures. The currently used methods are unable to predict accurately the equilibria for these high pressure systems (Cohen et al., 1969). In view of the inadequacy of the existing methods, it is felt necessary to have an improved method for the above systems.

The correlation of Prausnitz and Chueh (1968) has great prospects for predicting vapor liquid equilibria for light hydrocarbon systems, but its wide application has been hindered by the nonavailability of the required parameters. Besides the pure component properties, this method requires binary parameters at the operating temperatures. The binary parameters are preferably evaluated from the experimental binary vapor liquid equilibrium data. Unfortunately in many cases reliable binary data are not available at the temperatures of interest. A typical example is the methane-ethene binary for which no reliable data are available above 178°K, while for processing a number of multicomponent systems of practical interest, the above data are required.

Although some attempts have been made to estimate these parameters, the results are not satisfactory. The present work was undertaken to develop methods for estimating these parameters and to test the method of equilibria prediction for the temperature range of interest to the petrochemical industry.

CONCLUSIONS AND SIGNIFICANCE

New methods are presented for the estimation of binary parameters (Henry's constant and van Laar self-interaction parameter) required in the Chueh-Prausnitz correlation for the prediction of vapor liquid equilibria of hydrogen and light hydrocarbon systems. These estimation methods are more convenient and accurate compared to the other presently available methods.

The estimation methods in conjunction with the Chueh-Prausnitz correlation have been tested using a large number of experimental multicomponent vapor liquid equilibrium data in the temperature range 117 to 422°K. The statistical analysis shows that the reliability of the calculated *K*-values matches with the experimental accuracy.

While handling mixtures containing supercritical components, it is customary to treat the component as a solute and use the unsymmetric convention for defining the reference state fugacities if the operating temperature is above 0.93 times the critical temperature of the component. This treatment has been found to give unusually high deviations in the temperature range 178°K (0.93 *Tc* of methane) to 200°K (1.05 *Tc* of methane) for systems containing methane. By treating methane as solvent in the above temperature range the prediction is improved. Complete details of the estimation methods have been given. The methods are ready for use for systems containing heptane, hexane, *n*-pentane, *i*-pentane, *n*-butane, 1-butene, *i*-butane, propane, propene, ethane, ethene, methane, nitrogen, and hydrogen.

The new estimation methods will considerably increase the application of Chueh-Prausnitz correlation to the computation of high pressure vapor liquid equilibria and result in more reliable design of the separation systems handling hydrogen and light hydrocarbon systems.

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The method of Chao and Seader (1961) is widely used for prediction of vapor liquid equilibria in the petroleum and petrochemical industry. This method gives large deviations particularly at higher pressures, in the presence of supercritical components and near the critical region. The correlation of Prausnitz and Chueh (1968) is expected to be superior for the computation of vapor liquid equilibria of light hydrocarbon systems, but its wide application has been hindered by the scarcity of the binary constants at the operating temperatures. This method would undoubtedly find wide application if the binary constants can be conveniently estimated.

An attempt to estimate binary parameters (B) such as Henry's constant and van Laar interaction constant for the light hydrocarbon systems has been made by Funk and Prausnitz (1971). This estimation method is based on the observation that for a binary system the ratio (B_{exp}/B_{cal}) is a simple, continuous function of the reduced temperature (T/Tc_1). The calculated binary parameters (B_{cal}) are found out by using the validity of the Redlich-Kwong equation of state for mixtures in the liquid state. The estimation of B is made either by extrapolation of B_{exp}/B_{cal} versus T/Tc_1 curve or by choosing the curve for a chemically similar system. However, such curves may deviate appreciably from a straight line, particularly near the critical temperatures of the components. Hence this method is of limited value for extrapolation and for systems with little data. Recently Preston and Prausnitz (1971) have correlated Henry's constant $H_{2(1)}$ for nonpolar systems by an equation of the following form:

$$\ln \frac{H_{2(1)}^{(P_1^s)} v_1^s}{RT} = F\left(\frac{T}{Tc_2^\infty}, \frac{v_1^s}{vc_2^\infty}\right) \qquad (1)$$

To use this equation, 16 empirical constants and the characteristic binary constants Tc_2^∞ and vc_2^∞ are required.

In view of the great importance of the estimation methods and limitations of those presently known, the present study was undertaken to develop convenient correlations for estimating Henry's constants and van Laar interaction constants for hydrogen and light hydrocarbon systems.

DEVELOPMENT OF GENERALIZED CORRELATIONS

Henry's Constant

It was observed that plots of ln $H_{2(1)}$ versus $1/T$ for different systems have similar shape. Also the fugacity of pure liquids at zero pressure can be correlated in the following form (Prausnitz and Chueh, 1968):

$$\ln \frac{f^{(P0)}}{P_c} = C_0 + \frac{C_1}{T_r} + \frac{C_2}{T_r^2} + \frac{C_3}{T_r^3} + \frac{C_4}{T_r^4} \qquad (2)$$

Since $H_{2(1)}^{(P0)}$ can be regarded as fugacity of a solute in the solvent at zero pressure, it is expected that the reduced Henry's constant can be correlated as a polynomial of the following form:

$$\ln \frac{H_{2(1)}^{(P0)}}{P_h} = D_0 + \frac{D_1}{T_r} + \frac{D_2}{T_r^2} + \frac{D_3}{T_r^3} + \ldots . \qquad (3)$$

Available data of Henry's constants obtained from vapor liquid equilibria data reduction were collected from the work of Prausnitz and Chueh (1968) and additional binary vapor liquid equilibria data were processed to evaluate the Henry's constants for several other systems. Examination of the data revealed that Tc_2 is a good reducing parameter for temperature. Data for the methane-heptane binary system (Prausnitz and Chueh, 1968) are available over a wide temperature range. These data were processed to evaluate the constants of Equation (3) taking P_h equal to Pc_2 as a first approximation. Using the constants obtained above, the best fit P_h values were determined for different binary systems at various temperatures and were found to be slightly dependent on temperature. These values were fitted with linear or quadratic functions of T_r wherever the available data justified. For estimation in systems with little data, correlations of P_h (average over the temperature range) against ω_1 were developed for different solutes as shown in Figure 1.

The estimates of P_h were made by one of the following methods:

1. For the members of a homologous series with respect to a particular solute, temperature dependent values of P_h were estimated graphically wherever the data showed some definite trends.
2. For all other cases Figure 1 was used.

The final equations for the estimation of Henry's constant for light hydrocarbon systems are given below:

$$\ln \frac{H_{2(1)}^{(P0)}}{P_h} =$$

$$-3.333871 + \frac{11.43051}{T_r} - \frac{16.99066}{T_r^2} + \frac{6.619014}{T_r^3} \qquad (4)$$

The reducing parameter P_h is given by:

$$\ln P_h = a_0 + \frac{a_1}{T_r} + \frac{a_2}{T_r^2} \qquad (5)$$

The values of a_0, a_1, and a_2 for several systems are given in Table 1.

$$T_r = T/T_h \qquad (6)$$

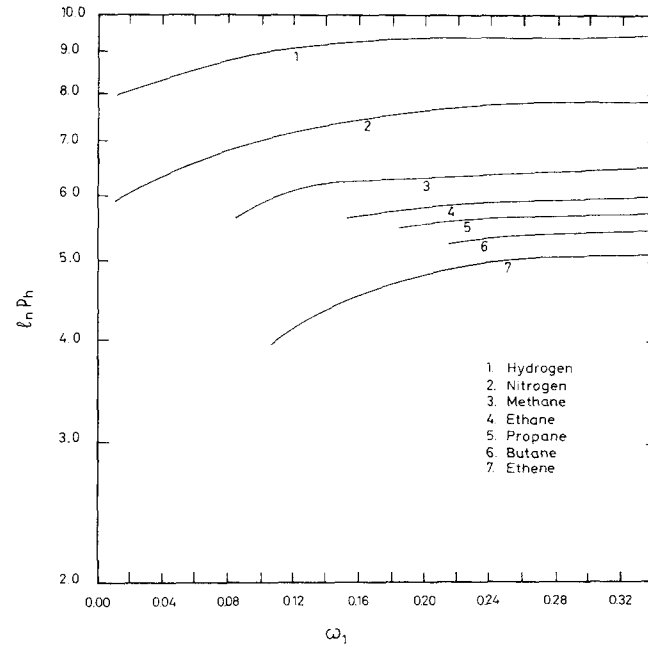

Fig. 1. Reducing parameter P_h for Henry's constants.

and

$$T_h = Tc_2 \tag{7}$$

In the presence of quantum gases T_h is given by

$$T_h = \frac{Tc_2}{1 + \dfrac{C}{M_{12}\,T}} \tag{8}$$

where M_{12} is the harmonic mean of the molecular weights of 1 and 2, and

$$C = 21.8°\text{K} \tag{9}$$

van Laar Parameters

Out of the two parameters required by the dilated van Laar model (Prausnitz and Chueh, 1968), the dilation constant η can be estimated according to the procedure proposed by Prausnitz and Chueh (1968). For the estimation of self-interaction constant α, a modified Hildebrand model has been used. For a binary mixture this model gives (Hildebrand et al., 1970)

$$RT \ln \gamma_1 = v_1 \phi_{s2}^2 [(\delta_1 - \delta_2)^2 + 2 l_{12} \delta_1 \delta_2] \tag{10}$$

$$RT \ln \gamma_2 = v_2 \phi_{s1}^2 [(\delta_1 - \delta_2)^2 + 2 l_{12} \delta_1 \delta_2] \tag{11}$$

where

$$\phi_{s1} = \frac{x_1 v_1}{x_1 v_1 + x_2 v_2} \tag{12}$$

$$\phi_{s2} = \frac{x_2 v_2}{x_1 v_1 + x_2 v_2} \tag{13}$$

and l_{12} is a characteristic constant for 1-2 interaction.

The activity coefficients in the symmetric and the unsymmetric conventions are related by the following equation

$$\gamma_2^* = \gamma_2/\gamma_2^\infty \tag{14}$$

Equating the values of activity coefficients given by the

Table 1. Reducing Parameters for Henry's Constants
$\ln P_h = a_0 + a_1/T_r + a_2/T_r^2$

System solvent	solute	a_0	a_1	a_2
Heptane	Hexane	5.44000	0.0	0.0
Heptane	Pentane	5.44000	0.0	0.0
Heptane	*i*-Pentane	5.44000	0.0	0.0
Heptane	Butane	−2.40085	17.23450	−9.43785
Heptane	Butene	5.44000	0.0	0.0
Heptane	*i*-Butane	5.44000	0.0	0.0
Heptane	Propane	6.79000	−1.21000	0.0
Heptane	Propene	5.18000	0.0	0.0
Heptane	Ethane	1.64660	10.83530	−6.63319
Heptane	Ethene	8.40000	−3.10000	0.0
Heptane	Methane	6.52093	−0.03328	0.02786
Heptane	Nitrogen	7.10000	1.05000	0.0
Heptane	Hydrogen	7.90000	6.00000	0.0
Hexane	Pentane	5.44000	0.0	0.0
Hexane	*i*-Pentane	5.44000	0.0	0.0
Hexane	Butane	5.44000	0.0	0.0
Hexane	Butene	5.44000	0.0	0.0
Hexane	*i*-Butane	5.44000	0.0	0.0
Hexane	Propane	6.71000	−1.12000	0.0
Hexane	Propene	5.33000	0.0	0.0
Hexane	Ethane	5.9600	0.0	0.0
Hexane	Ethene	8.40000	−3.10000	0.0
Hexane	Methane	5.98250	2.25719	−2.40651
Hexane	Nitrogen	6.69481	2.07097	−0.69012
Hexane	Hydrogen	5.60357	49.88570	−182.55800
Pentane	*i*-Pentane	5.44000	0.0	0.0
Pentane	Butane	5.44000	0.0	0.0
Pentane	Butene	5.44000	0.0	0.0
Pentane	*i*-Butane	5.44000	0.0	0.0
Pentane	Propane	1.48877	9.84699	−5.73213
Pentane	Propene	5.47000	0.0	0.0
Pentane	Ethane	5.91000	0.0	0.0
Pentane	Ethene	1.25460	10.42320	−5.83115
Pentane	Methane	1.81472	16.76659	−15.08140
Pentane	Nitrogen	6.69481	2.07097	−0.69012
Pentane	Hydrogen	8.40000	3.00000	0.0
i-Pentane	Butane	5.44000	0.0	0.0
i-Pentane	Butene	5.44000	0.0	0.0
i-Pentane	*i*-Butane	5.44000	0.0	0.0
i-Pentane	Propane	−5.86293	24.65999	−13.24110
i-Pentane	Propene	5.58000	0.0	0.0
i-Pentane	Ethane	5.86000	0.0	0.0
i-Pentane	Ethene	9.20000	−3.60000	0.0
i-Pentane	Methane	6.38000	0.0	0.0
i-Pentane	Nitrogen	6.70000	1.15000	0.0
i-Pentane	Hydrogen	8.50000	3.30000	0.0

Table 1. (Continued)

System solvent	solute	α_0	α_1	α_2
Butane	Butene	5.44000	0.0	0.0
Butane	*i*-Butane	5.44000	0.0	0.0
Butane	Propane	−4.05354	20.75200	−11.07300
Butane	Propene	6.81021	−2.36300	1.16695
Butane	Ethane	0.29199	12.78520	−7.35315
Butane	Ethene	−0.61897	14.08750	−7.55092
Butane	Methane	5.97584	0.66634	0.0
Butane	Nitrogen	6.55372	1.60166	−0.34059
Butane	Hydrogen	8.14802	6.92561	−8.42177
Butene	*i*-Butane	5.44000	0.0	0.0
Butene	Propane	7.19804	−2.63103	0.97728
Butene	Propene	5.65000	0.0	0.0
Butene	Ethane	5.60800	0.24000	0.0
Butene	Ethene	11.19600	−5.26300	0.0
Butene	Methane	6.93000	−0.35000	0.0
Butene	Nitrogen	6.50000	1.25000	0.0
Butene	Hydrogen	8.50000	5.86000	0.00
i-Butane	Propane	6.52000	−0.92000	0.0
i-Butane	Propene	5.66000	0.0	0.0
i-Butane	Ethane	5.79000	0.0	0.0
i-Butane	Ethene	9.80000	−4.20000	0.0
i-Butane	Methane	6.33000	0.0	0.0
i-Butane	Nitrogen	6.50000	1.25000	0.0
i-Butane	Hydrogen	8.50000	3.50000	0.0
Propane	Propene	13.23560	−5.61438	0.0
Propane	Ethane	−8.14107	29.47780	−15.70900
Propane	Ethene	−1.56558	15.57980	−8.30491
Propane	Methane	3.04843	8.00786	−4.84945
Propane	Nitrogen	6.41685	0.92979	0.28755
Propane	Hydrogen	8.20000	3.80000	0.0
Propene	Ethane	4.76245	2.04272	−0.95976
Propene	Ethene	−1.47331	15.72430	−8.39518
Propene	Methane	4.06486	5.62863	−3.44878
Propene	Nitrogen	6.48781	0.72509	0.45640
Propene	Hydrogen	7.69817	9.81985	−7.84251
Ethane	Ethene	13.40000	−7.40000	0.0
Ethane	Methane	3.48419	6.16655	−3.70935
Ethane	Nitrogen	4.44931	6.16671	−3.40287
Ethane	Hydrogen	7.24169	9.33627	−9.32254
Ethene	Methane	4.34860	4.22961	−2.88004
Ethene	Nitrogen	5.67727	2.56034	−1.30943
Ethene	Hydrogen	6.69000	13.12570	−13.80490
Methane	Nitrogen	2.38787	8.78830	−5.31248
Methane	Hydrogen	6.34673	4.77648	0.0
Nitrogen	Hydrogen	4.48906	7.13905	−3.81567

modified Hildebrand and the dilated van Laar model, the following relationships are obtained

(i) Symmetric Convention $T < 0.93\ Tc_2$

$$\ln \gamma_2^{(P0)} = \frac{v_2}{RT}\left[(\delta_1 - \delta_2)^2 + 2\, l_{12}\, \delta_1\, \delta_2\right] \phi_{s_1}^2$$

$$= vc_2\, \alpha_{12}\, \phi_{c_1}^2 \qquad (15)$$

(ii) Unsymmetric Convention $T \geqq 0.93\ Tc_2$

$$\ln \gamma_2^{*(P0)} = \frac{v_2}{RT}\left[(\delta_1 - \delta_2)^2 + 2\, l_{12}\, \delta_1\, \delta_2\right] (\phi_{s_1}^2 - 1)$$

$$= vc_2\, \alpha_{22(1)}\, [\phi^2{}_{c_2} - 2\phi_{c_2}]$$

$$+ 3\eta_{2(1)}\, \alpha_{22(1)}\, vc_2 \left(\phi_{c_2}^4 - \frac{4}{3}\phi_{c_2}^3\right) \qquad (16)$$

where

$$\phi_{c_1} = \frac{x_1 vc_1}{x_1 vc_1 + x_2 vc_2} \qquad (17)$$

and

$$\phi_{c_2} = \frac{x_2 vc_2}{x_1 vc_1 + x_2 vc_2} \qquad (18)$$

The l_{12} values were calculated by substituting self-interaction constants, reported by Prausnitz and Chueh (1968), or obtained by data reduction of binary vapor liquid equilibrium data, in Equation (15) or (16) at low solute concentrations where the effect of the term containing $\eta_{2(1)}$ is small. The l_{12} values so obtained after some smoothing have been fitted in a manner similar to that used for correlating the Henry's constants. The resulting generalized equation is

$$\frac{l_{12}}{P_a} = 0.92540562 - 3.3223918\, R + 2.476714\, R^2$$

$$-0.37223283\, R^3 + 6.4160495/R - 15.712184/R^2$$

$$- 4.9479723 \ln (R - 0.9) \qquad (19)$$

A plot of the above function is given in Figure 2. It may be noted that the curve is very similar to the generalized plot of η versus T (Prausnitz and Chueh, 1968). In Equation (19),

$$R = T_a/T \qquad (20)$$

Correction of T_a for the presence of quantum gases is similar to that of T_h. Parameters T_a and P_a are characteristic of the binary system and have been correlated against the acentric factors of the components by the following equations

$$\ln P_a = 3.70988 - 11.4649\, \omega_1 - 4.41237\, \omega_2$$

$$+ 49.8516\, \omega_1^2 - 128.881\, \omega_1\omega_2 - 117.526\, \omega_2^2$$

$$- 91.5182\, \omega_1^3 + 142.191\, \omega_1^2\omega_2 + 188.036\, \omega_1\omega_2^2$$

$$+ 45.9346\, \omega_2^3 \qquad (21)$$

$$\ln (T_a/P_a) = 2.50593 + 20.2731\, \omega_1 + 10.0422\, \omega_2$$

$$- 87.9087\, \omega_1^2 + 70.6034\, \omega_1\omega_2 + 136.247\, \omega_2^2$$

$$+ 144.032\, \omega_1^3 - 5.99945\, \omega_1^2\omega_2$$

$$- 291.673\, \omega_1\omega_2^2 - 9.27736\, \omega_2^3 \qquad (22)$$

For the estimation of self-interaction constants, the procedure outlined above may be reversed. The l_{12} values are estimated by using Equations (19) to (22). Knowing η and l_{12}, self-interaction constants may be calculated using Equation (15) or (16).

PREDICTION OF MULTICOMPONENT PHASE EQUILIBRIA

Experimental phase equilibrium data were used to ascertain the accuracy of estimation methods developed. For the above purpose, the temperature and liquid compositions corresponding to the data points were taken. The pressure and vapor compositions were calculated by a bubble point computation procedure and compared with the experimental values. While handling mixtures containing supercritical components, it is customary to treat a component as solute and use the unsymmetric convention if the operating temperature is above 0.93 times the critical temperature of the component. However, for methane a slightly different treatment is recommended. The considerable improvement in prediction by treating methane as a solvent component up to 200°K is evident from the

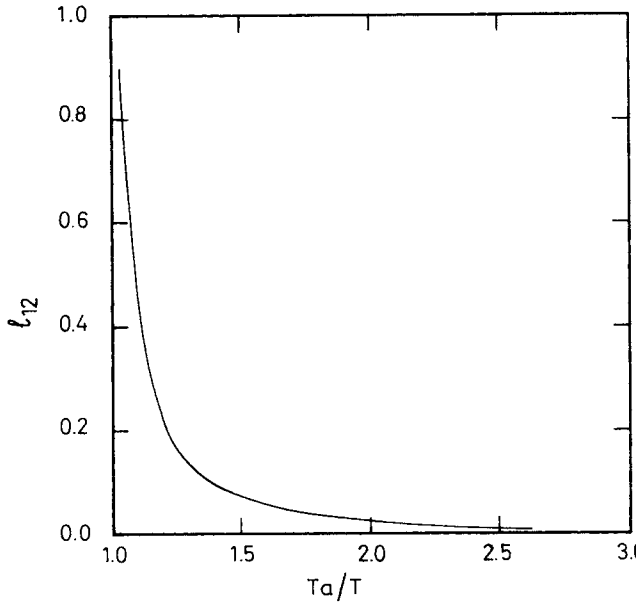

Fig. 2. Correlation of l_{12}.

Table 2. Summary of % Absolute Average Deviations of K-Values
(Based on data published during 1959-1971)

Exp. data ref.	Temp. range °K	°K	No. of pts.	n-C_5-H_{12}	n-C_4-H_{10}	C_3H_8	C_2H_6	C_2H_4	C_1H_4	H_2
Herlihy and Thodos (1962)	339	422	33	6.1	5.0		1.1			
Cohen et al. (1967)	117	256	85				7.1		16.1	3.5
Rigas et al. (1959)	311		15		9.4	3.8			1.1	
Price and Kobayashi (1959)	200	284	107			8.5	5.4		2.0	
Cohen et al. (1969)	117	256	94				4.4	6.9	15.5	3.4
Wiese et al. (1970)	278	378	55		5.1	4.5			2.1	
	117	422	389	6.1	5.7	6.9	5.1	6.9	8.9	3.4

Table 4. Results of Prediction for n-C_4H_{10}-C_3H_8-C_2H_6-C_1H_4-N_2 System

Temp., °K	Pressure, atm.	Comp	x	y_{cal}	y_{exp}	Devn. %
183.0	25.2	n-C_4H_{10}	0.0162	0.0000	0.0000	0.0
		C_3H_8	0.0491	0.0006	0.0009	−27.9
		C_2H_6	0.2267	0.0210	0.0202	4.0
		C_1H_4	0.7060	0.9645	0.9667	−0.2
		N_2	0.0020	0.0138	0.0122	13.4
180.5	25.2	n-C_4H_{10}	0.0105	0.0000	0.0000	0.0
		C_3H_8	0.0339	0.0004	0.0006	−35.6
		C_2H_6	0.1777	0.0153	0.0151	1.1
		C_1H_4	0.7750	0.9662	0.9702	−0.4
		N_2	0.0030	0.0181	0.0140	29.5
178.0	25.2	n-C_4H_{10}	0.0183	0.0000	0.0000	0.0
		C_3H_8	0.0208	0.0002	0.0003	−30.0
		C_2H_6	0.1140	0.0091	0.0088	4.0
		C_1H_4	0.8433	0.9706	0.9742	−0.4
		N_2	0.0037	0.0200	0.0168	19.3

Table 7. Effect of Treating Methane by Different Conventions
% Absolute Average Deviations of K-Values

Exp. data ref.	Temp. °K	No. of points		C_2H_6	C_2H_4	C_1H_4	H_2
Kogan et al. (1966)	178	26	a		93.3	27.5	25.5
			b		21.6	15.2	5.0
Kogan et al. (1966)	188	20	a		104.7	23.2	28.0
			b		21.1	5.8	8.4
Cohen et al. (1969)	200	24	a	60.0	12.9	29.3	21.5
			b	8.7	10.2	9.4	6.7

[a] Methane treated as a solute component.
[b] Methane treated as a solvent component.

sample results presented in Table 7. Tables 2 and 3* give the average deviations of predicted K-values from the experimental for the different components. In the tables 689 data points that converged with the reduced temperature of the mixture below 0.93 have been included. Table 2 contains the systems published during 1959 to 1971. It may be noted that the average deviation for hydrogen and light hydrocarbons is less than 10%. Results on several other systems based on the data published prior to 1959 are also included in Table 3. In this table data have been grouped by temperatures. It is interesting to observe that even in the earlier data, in the entire temperature range investigated 117 to 422°K, the prediction is satisfactory for hydrogen and light hydrocarbons. For nitrogen the deviation is somewhat larger but comparable to the better prediction methods. It should be kept in mind that the accuracy of the experimental measurements greatly depends on the concentration of the component. For example, Cohen et al. (1969) indicate the following accuracies for their analysis:

Concentration	Accuracy
0.05%	± 50%
1.0%	± 10%
Higher	± 3%

Examination of the individual data points revealed that the deviation of the K-values can be explained by the reliability of the experimental measurements in most cases. To cite an example, some recent data from E.I.L. files are presented in Table 4. Although the deviation for C_3H_8 is about 30%, it is noted that its concentration is of the order of 0.05% in the vapor and about 3% in the liquid phase. The calculated vapor compositions are well within the range of accuracy (50%) of the experimental values. Nitrogen presents a similar situation.

In Tables 5* and 6*, a comparison of the present method with other currently used prediction methods has been made. Deviations for different methods were taken from the work of Cohen et al. (1967, 1969) and the present method has been applied to the data of Cohen. The superiority of the present method is obvious from the tables.

CONCLUSION

New methods have been presented for the estimation of binary parameters (Henry's constant and van Laar parameter) used in the Chueh-Prausnitz correlation for the prediction of vapor liquid equilibria of light hydrocarbon systems. These estimation methods are more convenient and accurate compared to the other presently available methods.

In using the unsymmetric convention for defining standard state fugacity, methane should be treated as solvent up to 200°K.

Experimental multicomponent data were tested using the estimation methods in conjunction with the Chueh-Prausnitz correlation. The reliability of the calculated K-values for hydrogen and light hydrocarbons matches with the experimental accuracy in the entire temperature range tested 117 to 422°K.

The new estimation methods for Henry's constant and van Laar interaction parameter will undoubtedly lead to

* Tables 3, 5 and 6 have been deposited as Document No. 01861 with National Auxiliary Publications Service (NAPS), c/o CCM Information Corp., 866 Third Ave., New York 10022 and may be obtained for $2.00 for microfiche or $5.00 for photocopies.

the increased application of the Chueh-Prausnitz method for vapor liquid equilibria prediction of high pressure systems.

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NOTATION

B = binary parameter
f = fugacity
F = a particular function
$H_{2(1)}$ = Henry's constant for solute 2 in solvent 1, atm.
l_{12} = characteristic constant for 1-2 interaction
M_{12} = harmonic mean molecular weight of 1 and 2
Pc = critical pressure, atm.
P_a, P_h = reducing parameters
R = gas constant
T = temperature, °K
Tc = critical temperature, °K
T_a, T_h = reducing parameters
T_r = reduced temperature
v = molar volume
vc = critical volume
x = mole fraction in the liquid phase
y = mole fraction in the vapor phase

Greek Letters

$\alpha_{22(1)}$ = self-interaction constant of molecules 2 in the environment of molecules 1
α_{12} = interaction constant of molecules 1 and 2
γ = activity coefficients for solvent components
γ^* = activity coefficients for solute components (in unsymmetric convention)
δ = solubility parameter
η, $\eta_{2(1)}$ = dilation constant of solute 2 in solvent 1
ϕ = volume fraction as given by Equations (12), (13), (17), (18)
ω = acentric factor

Superscripts

$(P0)$ = at constant reference pressure of zero pressure
$(P_1{}^s)$ = at the saturation pressure of component 1, the solvent
s = at saturation
$*$ = unsymmetric convention of normalization for activity coefficients
∞ = infinite dilution

Subscripts

1 = solvent
2 = solute
a = for self-interaction constant
c = critical
cal = calculated
exp = experimental
i = component i
$ii(j)$ = i-i interaction in the environment of j
ij = i-j interaction
h = for Henry's constant
r = reduced quantity
s = saturated liquid property

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