

Prediction of Vapor-liquid Equilibrium Data for Binary Hydrocarbon Mixtures at Various Total Pressures

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An empirical method is suggested which permits the prediction of vapor-liquid equilibrium data for binary hydrocarbon mixtures at various total pressures on the basis of equilibrium data at one constant pressure. This method has been tested with the vapor-liquid equilibrium data of six nonideal systems measured at twenty-one different experimental conditions. The total pressure range varies from 50 mm. of mercury to 4 atm. In all cases the predicted results are in good agreement with the experimental data.

Data on vapor-liquid equilibrium are of great interest to chemical industries employing fractional distillation. In the literature a number of methods for representation of vapor-liquid equilibrium data have been suggested and reviewed (1, 2, 6, 7, 11), some of which have been useful for predicting or extrapolating x - y data. Recently Wehe and Coates (15) suggested a method for correlation of activity coefficients. Their method allows data taken on systems for which experimental results are available to be used to predict those for other systems on which only the boiling points of the pure components are available. They have predicted, for example, the x - y curve for the system benzene- n -butanol with the vapor-liquid equilibrium data of the systems benzene-methanol, benzene-ethanol, and benzene- n -propanol used as primary information. Spinner, Lu, and Graydon (12) suggested an empirical method which permits the prediction of the binary vapor-liquid equilibrium data (component 1-component 2) on the basis of other binary data for the two components, each with some third component (component 1-component 3 and component 2-component 3), and of ternary vapor-liquid equilibrium data with equilibrium data for two of the three binary systems used as primary information.

To date full advantage has not been taken of data existing in the literature. The empirical method described in this paper extends the use which can be made of these available data by permitting the prediction of vapor-liquid equilibrium data for binary hydrocarbon mixtures at various total pressures if the equilibrium data at one constant pressure are known.

ALGEBRAIC METHOD

For binary systems Clark (2) suggested that the ratio of the mole fractions in one phase is a linear function of the ratio of the mole fractions in the other phase

when the ratios are used such that the components in larger amounts appear in the numerator. Thus, for high values of x_1

$$y_1/y_2 = ax_1/x_2 + b \quad (1a)$$

and for high values of x_2 ,

$$y_2/y_1 = a'x_2/x_1 + b' \quad (1b)$$

where x and y refer to mole fractions in the liquid and vapor, respectively. The quantities a , a' , b , and b' are constants. Subscripts 1 and 2 refer to more and less volatile components, respectively. In order that the entire system may be continuously represented by these two equations, it is necessary that Equations (1a) and (1b) have a point of contact at some values of x between 0 and 1.0 where dy/dx are identical from both equations. This condition is satisfied when

$$(aa')^{1/2} \pm (bb')^{1/2} = 1 \quad (2)$$

The sign of the quantities b and b' and the term $(bb')^{1/2}$ is taken to be the sign of the quantity $[1 - (aa')^{1/2}]$. At the tangent point

$$x_1 = \frac{(a'b/ab')^{1/2}}{1 + (a'b/ab')^{1/2}} = D \quad (3)$$

For an ideal case, where Raoult's law is obeyed,

$$a = 1/a' = \alpha$$

and

$$b = b' = 0$$

where α is the relative volatility.

Equations (1a) and (1b) were used in this study and found to be excellent representations of the vapor-liquid equilibrium data for binary hydrocarbon mixtures.

The constants a and a' of Equations (1a) and (1b) may be expressed in the following manner,

$$a = (P_1^0/P_2^0)_T \exp(-A) \quad (4a)$$

and

$$a' = (P_2^0/P_1^0)_T \exp(-B) \quad (4b)$$

where $(P_1^0/P_2^0)_T$ represents the ratio

of the vapor pressures of the pure components at the boiling point of pure component 1 and $(P_1^0/P_2^0)_T$ represents the ratio of the vapor pressures of the pure components at the boiling point of pure component 2. A and B are constants.

Ewell, Harrison, and Berg (3) have explained deviations of nonideal systems in terms of the hydrogen-bonding characteristics of the components. They have classified all binary hydrocarbon mixtures as "quasiideal" systems which always indicate positive deviations (the values of the activity coefficients are above unity) or follow Raoult's law. The constants A and B of Equations (4a) and (4b) are positive numbers for positive deviations and zero for ideal systems. The method of prediction described in this paper is limited to the foregoing conditions.

PREDICTION OF THE CONSTANTS a AND a'

With the constants A and B obtained from the known vapor-liquid equilibrium data of the same system at one constant pressure used as primary information, the following empirical relations are proposed for the prediction of constants A and B of Equations (4a) and (4b) for a system at various total pressures:

$$A_\pi = A \frac{1 + C(\pi_K)^{1/2}}{1 + C(\pi)^{1/2}} \quad (5a)$$

$$B_\pi = B \frac{1 + C(\pi_K)^{1/2}}{1 + C(\pi)^{1/2}} \quad (5b)$$

where

A and B refer to the constants, calculated from Equations (4a) and (4b) for the known vapor-liquid equilibrium data at total pressure π_K ,

A_π and B_π refer to the constants for the same system at total pressure π

π_K refers to the total pressure under which the known vapor-liquid equilibrium data were determined

π refers to the total pressure under which the vapor-liquid equilibrium data are being predicted

C is a dimension-correcting constant.

If the units of π_K , π , and C are taken to be atm., atm., and (atm.)^{-1/2} respectively, then C is unity. Hence the constants a and a' of Equations (1a) and (1b) at various total pressures may be calculated by the following equations:

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$$a = (P_1^0/P_2^0)_{T_{1*}} \cdot \exp \left\{ -A \frac{1 + C(\pi_K)^{1/2}}{1 + C(\pi)^{1/2}} \right\}$$

and

$$a' = (P_2^0/P_1^0)_{T_{2*}} \cdot \exp \left\{ -B \frac{1 + C(\pi_K)^{1/2}}{1 + C(\pi)^{1/2}} \right\}$$

where T_{1*} and T_{2*} refer to the boiling points of components 1 and 2, respectively, at total pressure π .

EVALUATION OF THE CONSTANTS b AND b'

After the constants a and a' have been obtained, two equations are required to evaluate the constants b and b' of Equations (1a) and (1b). Equation (2) provides one of them. The Redlich and Kister (10) relationship may be combined with Equations (1a) and (1b) to provide the other.

By definition,

$$\alpha = (P_1^0/P_2^0)(\gamma_1/\gamma_2)$$

where γ refers to the activity coefficients.

$$\int_0^1 \log \alpha dx_1 = \int_0^1 \log (P_1^0/P_2^0) dx_1 + \int_0^1 \log (\gamma_1/\gamma_2) dx_1$$

Assuming that the vapor phase is an ideal gas mixture and the activity coefficients are independent of temperature, Redlich and Kister have derived that

$$\int_0^1 \log (\gamma_1/\gamma_2) dx_1 = 0$$

Therefore,

$$\int_0^1 \log \alpha dx_1 = \int_0^1 \log (P_1^0/P_2^0) dx_1 \quad (6)$$

The right-hand side of Equation (6) may be taken as

$$\frac{1}{2} [\log (P_1^0/P_2^0)_{T_1} + \log (P_1^0/P_2^0)_{T_2}]$$

Equation (1) may be rearranged to give

$$\alpha = [ax_1 + b(1 - x_1)]/x_1 \quad \text{for } D \leq x_1 \leq 1$$

$$\alpha = (1 - x_1)/[x_1(b' - a') + a'] \quad \text{for } D \geq x_1 \geq 0$$

where D refers to the value of x_1 at the tangent point as defined by Equation (3). Hence,

$$\frac{1}{2} [\log (P_1^0/P_2^0)_{T_1} + \log (P_1^0/P_2^0)_{T_2}] = \int_0^1 \log \alpha dx_1$$

$$\begin{aligned} &= \int_0^D \log \left\{ \frac{1 - x_1}{x_1(b' - a') + a'} \right\} dx_1 + D \log D \\ &\quad + \int_D^1 \log \left\{ \frac{ax_1 + b(1 - x_1)}{x_1} \right\} dx_1 - (1 - D) \log (1 - D) \quad (7) \\ &= \frac{a}{a - b} \log a + \frac{a'}{b' - a'} \log a' \\ &\quad - \left\{ \frac{(a - b)D + b}{a - b} \right\} \cdot \log [(a - b)D + b] \\ &\quad - \left\{ \frac{(b' - a')D + a'}{b' - a'} \right\} \cdot \log [(b' - a')D + a'] \end{aligned}$$

Equations (2) and (7) may be used to evaluate the constants b and b' . This method involves a trial-and-error calculation.

As a first approximation, the constants b and b' were calculated by means of Equations (2) and (8), with Equation (7) used to check the validity of this approximation.

$$b/b' = d/d' \quad (8)$$

where

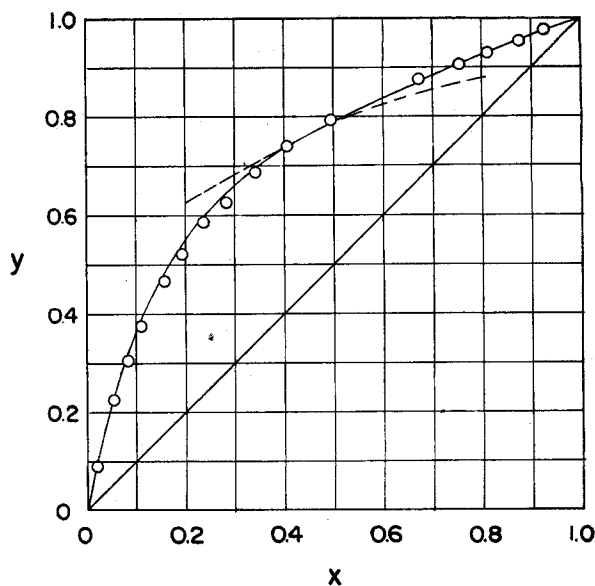


Fig. 1. Predicted vapor-liquid equilibrium curve and data (6) for system heptane-ethylbenzene, at 100 mm. Hg. \circ experimental; — predicted.

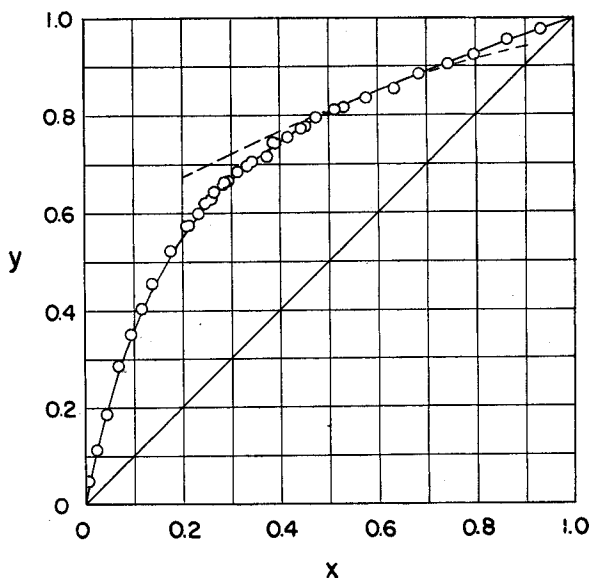


Fig. 2. Predicted vapor-liquid equilibrium curve and data (6) for system hexane-toluene, at 300 mm. Hg. \circ experimental; — predicted.

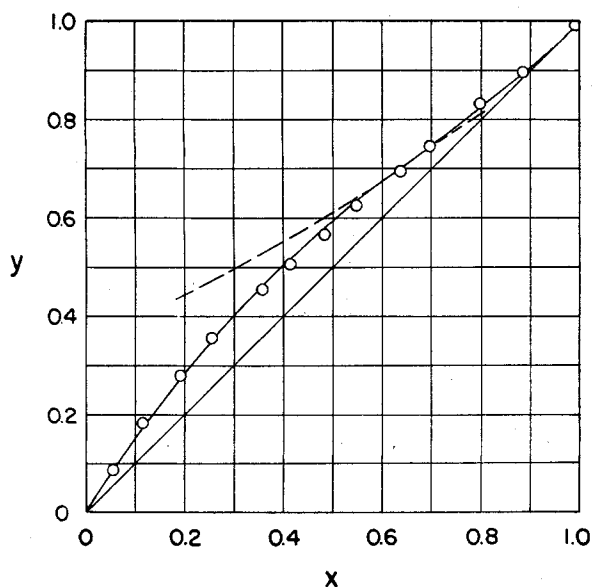


Fig. 3. Predicted vapor-liquid equilibrium curve and data (14) for system methylcyclohexane-toluene, at 400 mm. Hg. \circ experimental; — predicted.

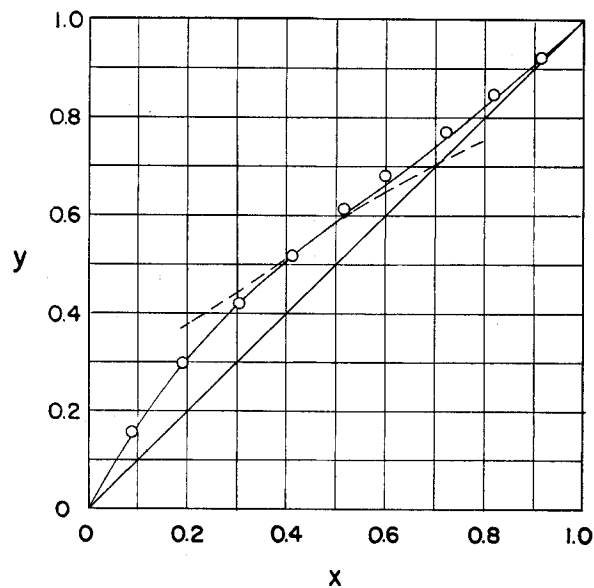


Fig. 5. Predicted vapor-liquid equilibrium curve and data (16) for system octane-ethylbenzene, at 50 mm. Hg. \circ experimental; — predicted.

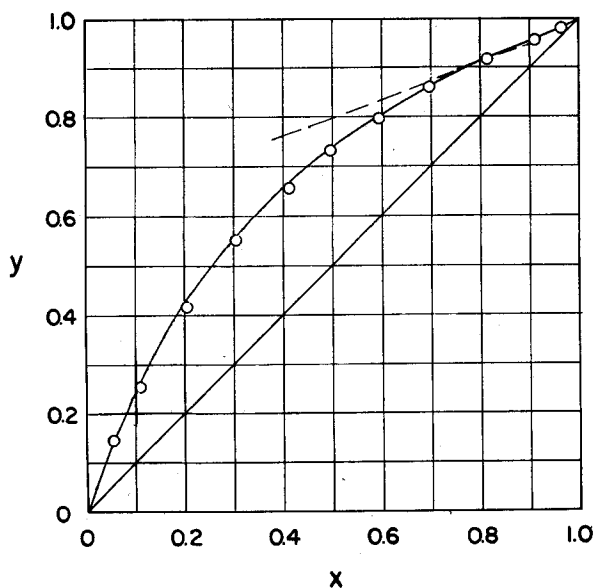


Fig. 4. Predicted vapor-liquid equilibrium curve and data (5) for system naphthalene-tetradecane, at 200 mm. Hg. \circ experimental; — predicted.

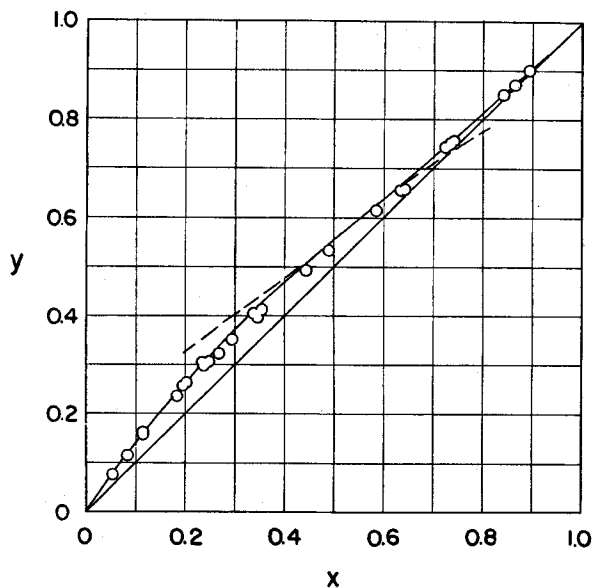


Fig. 6. Predicted vapor-liquid equilibrium curve and data (4) for system 2,2,4-trimethylpentane-toluene, at 4.06 atm. \circ experimental; — predicted.

$$d = -\frac{4.606a \{ \log [(P_1^0/P_2^0)_{T_1}/a] \}^2}{\log [a'(P_1^0/P_2^0)_{T_1}]} \quad (9a)$$

$$d' = \frac{4.606a' \{ \log [a'(P_1^0/P_2^0)_{T_1}] \}^2}{\log [(P_1^0/P_2^0)_{T_1}/a]} \quad (9b)$$

Equations (9a) and (9b) were derived by the combination of Equation (1) and Van Laar equations, as rearranged by Carlson and Colburn (1), at the limit concentrations ($x_1 \rightarrow 1$ and $x_1 \rightarrow 0$). Complete derivations have been given by Clark (2). Since good agreements were obtained as shown in Table 2 (columns 10 and 11), a second approximation was not required.

This method of prediction has been tested with the vapor-liquid equilibrium

data of six nonideal systems measured at twenty-one experimental conditions. The total-pressure range varies from 50 mm. Hg to 4 atm. The vapor-liquid equilibrium data of these systems at 1-atm. pressure were used as primary information. The vapor-pressure data used in this study were taken from the compilation of Stull (13). All the primary information used for prediction is listed in Table 1. The predicted values of the constants a , a' , b , and b' of these systems at various total pressures are listed in Table 2. The precision of this method of prediction is illustrated in Figures 1 to 6. The dotted lines on these graphs indicate the courses of the calculated curves when they are projected beyond the tangent point in the directions in which they become invalid. In all cases the predicted

results are in good agreement with the experimental data.

SAMPLE CALCULATION

The prediction of vapor-liquid equilibrium data for the system heptane-ethylbenzene at a pressure of 100 mm. Hg, on the basis of the vapor-liquid equilibrium data at 1-atm. pressure, illustrates the calculation.

At 1-atm. pressure,

$$a = 2.34$$

$$a' = 0.276$$

$$(P_1^0/P_2^0)_{T_1} = 3.10$$

$$(P_1^0/P_2^0)_{T_2} = 2.62$$

$$a = 2.34 = 3.10 \exp(-A)$$

$$\therefore A = 0.282$$

TABLE 1. PRIMARY INFORMATION FOR PREDICTION

System	Total pressure, atm.	a	a'	A	B	$\left(\frac{P_1^0}{P_2^0}\right)_{T_1}$	$\left(\frac{P_1^0}{P_2^0}\right)_{T_2}$	$T_1, ^\circ\text{C.}$	$T_2, ^\circ\text{C.}$
1. Heptane-ethylbenzene (6)	1	2.34	0.276	0.282	0.326	3.10	2.62	98.4	136.2
2. Hexane-toluene (6)	1	2.65	0.228	0.390	0.300	3.92	3.25	68.7	110.6
3. Methylcyclohexane-toluene (9)	1	1.040	0.650	0.249	0.157	1.332	1.316	100.9	110.6
4. Naphthalene-tetradecane (5)	1	1.780	0.428	0.290	0.106	2.38	2.10	217.9	252.5
5. Octane-ethylbenzene (16)	1	1.116	0.616	0.182	0.199	1.338	1.328	125.6	136.2
6. 2, 2, 4-Trimethylpentane-toluene (4)	1	1.040	0.540	0.300	0.282	1.403	1.395	99.2	110.6

Since this value is in good agreement with

$$\frac{1}{2}[\log(P_1^0/P_2^0)_{T_1} + \log(P_1^0/P_2^0)_{T_2}] = 0.584$$

a second approximation is not required. The predicted vapor-liquid equilibrium curve and data (6) for this system are illustrated in Figure 1.

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TABLE 2. PREDICTED CONSTANTS AT VARIOUS TOTAL PRESSURES

System	Total pressure	a	a'	b	b'	$\left(\frac{P_1^0}{P_2^0}\right)_{T_1}$	$\left(\frac{P_1^0}{P_2^0}\right)_{T_2}$	$T_1, ^\circ\text{C.}$	$T_2, ^\circ\text{C.}$	$\left[\log\left(\frac{P_1^0}{P_2^0}\right)_{T_1} + \log\left(\frac{P_1^0}{P_2^0}\right)_{T_2}\right]/2$	$\int_0^1 \log \alpha dx_1$
	mm. Hg										
1. Heptane-ethylbenzene (6)	100	2.78	0.177	0.960	0.0931	4.20	3.51	41.8	74.1	0.584	0.588
	300	2.53	0.220	0.676	0.0954	3.57	3.05	69.7	104.7	0.519	0.516
2. Hexane-toluene (6)	150	4.00	0.165	1.367	0.0256	6.88	4.00	24.8	61.9	0.720	0.706
	300	2.89	0.201	1.348	0.0425	4.68	3.45	41.9	80.9	0.604	0.594
3. Methylcyclohexane-toluene (14)	200	1.050	0.575	0.607	0.0819	1.459	1.415	59.6	69.5	0.157	0.165
	400	1.041	0.611	0.536	0.0765	1.388	1.361	79.6	89.5	0.138	0.138
4. Naphthalene-tetradecane (5)	50	2.50	0.284	2.10	0.0118	3.97	2.98	124.9	158.5	0.537	0.511
	100	2.19	0.306	2.21	0.0150	3.36	2.80	145.5	178.5	0.487	0.475
	200	2.005	0.338	1.94	0.0162	2.94	2.57	167.7	201.8	0.439	0.425
	400	1.87	0.378	1.611	0.0159	2.62	2.34	193.2	226.8	0.394	0.380
5. Octane-ethylbenzene (16)	50	1.072	0.509	0.332	0.204	1.435	1.430	49.9	57.7	0.156	0.147
	200	1.095	0.559	0.267	0.178	1.389	1.375	83.6	92.7	0.141	0.146
	500	1.111	0.600	0.219	0.153	1.361	1.341	111.2	121.3	0.131	0.131
	atm.										
6. 2, 2, 4-Trimethylpentane-toluene (4)	2.02	1.040	0.617	0.284	0.139	1.334	1.283	125.8	136.9	0.117	0.116
	4.06	1.034	0.670	0.228	0.122	1.261	1.238	157.7	168.6	0.097	0.097

$$a' = 0.276 = (1/2.62) \exp(-B)$$

$$\therefore B = 0.326$$

At 100 mm. Hg,

$$\frac{1 + C(\pi_R)^{1/2}}{1 + C(\pi)^{1/2}} = \frac{2}{1 + 0.362} = 1.47$$

$$(P_1^0/P_2^0)_{T_1} = 4.20$$

$$(P_1^0/P_2^0)_{T_2} = 3.51$$

$$a = 4.20 \exp(-0.282 \times 1.47)$$

$$= 2.78$$

$$a' = (1/3.51) \exp(-0.326 \times 1.47)$$

$$= 0.177$$

Use of Equations (9a) and (9b) gives

$$d = -4.606 \times 2.78$$

$$\times \frac{[\log(4.20/2.78)]^2}{\log(3.51 \times 0.177)}$$

$$= 2.00$$

$$d' = 4.606 \times 0.177$$

$$\times \frac{[\log(3.51 \times 0.177)]^2}{\log(4.20/2.78)}$$

$$= 0.194$$

Therefore,

$$b/b' = d/d' = 2.00/0.194 = 10.3$$

Use of Equation (2) gives

$$(aa')^{1/2} \pm (bb')^{1/2} = 1$$

$$(aa')^{1/2} = (2.78 \times 0.177)^{1/2} = 0.701$$

$$(bb')^{1/2} = 1 - 0.701 = 0.299$$

$$\therefore b = 0.960$$

$$\therefore b' = 0.0931$$

Substituting the values of a , a' , b , and b' into Equation (7) yields

$$\int_0^1 \log \alpha dx_1 = 0.588$$

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