Prediction of Vapor-Liquid Equilibria of Binary Systems: Part I. Effect of Pressure on Vapor-Liquid Equilibria of Binary Systems

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This paper presents an empirical method for the prediction of vapor-liquid equilibrium data of a binary system at various pressures on the basis of equilibrium data near atmospheric pressure. The proposed method is tested for six hydrocarbon systems and one aqueous system. The calculated results are in good agreement with the experimental data.

In the design of distillation equipment an accurate and complete knowledge of vapor-liquid equilibrium data is indispensable. Most of the vapor-liquid equilibrium data published to date are obtained under atmospheric pressure, and the experimental data at various different pressures are still limited in number. Accordingly it is especially convenient for engineering purposes to find the methods for predicting the x-y correlation at every different pressure on the basis of the known data at a given pressure. This problem, in principle, may be solved by means of the thermodynamic relationship. However, this approach would need painstaking efforts, for example the determination of the temperature dependence of the activity coefficients.

The present method, though empirical, makes it possible to predict the x-y correlation of a binary system at various pressures, if the x-y data at an arbitrary pressure near atmospheric is given. The method can avoid complexities accompanied with the thermodynamic treatment of the activity coefficients. Recently Lu (*10*) proposed an empirical method similar to the one proposed here.

PROPOSED METHOD

Algebraic equations expressing the relation between vapor composition and liquid composition are useful for distillation calculations. Several investigators have proposed different forms (*6*). The equation originally proposed by Prahl (*14*) is extremely useful for its simple and flexible form, which recently Lu, Li, and Ting (*11*) have rederived and arranged by using the cluster theory and extended to comprise ternary systems. One of the present authors (*13*) has further extended it to include the boiling points of binary and ternary systems. Hence the present method is based on the following Prahl equation:

$$\frac{y_1}{y_2} = \frac{x_1}{x_2}\left(\frac{a_{12}x_1 + a_0 x_2}{a_{21}x_2 + x_1}\right) \qquad (1)$$

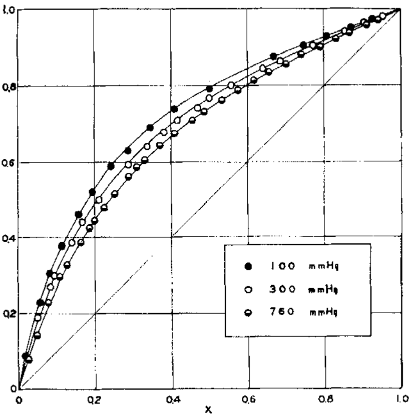

Fig. 1. Predicted and experimental vapor-liquid equilibrium for *n*-heptane-ethylbenzene system (*10*): ———— predicted, o experimental.

Equation (1) represents the x-y correlation of many binary systems with sufficient accuracy. The constants a_{12}, a_0 and a_{21} in Equation (1) are not independent of one another. The authors have derived the following relations, applying Clark's method (*2*) to Equation (1):

$$a_{12} = (P_1/P_2)_{t_1} \exp(-A_0) \qquad (2)$$

$$a_{21}/a_0 = (P_2/P_1)_{t_2} \exp(-B_0) \qquad (3)$$

$$\begin{aligned} a_0 &= [a_{12}(a_0/a_{21})(A_0/B_0)^3]^{1/2} \\ &= [(P_1/P_2)_{t_1}(P_1/P_2)_{t_2}(A_0/B_0)^3 \exp(-A_0 + B_0)]^{1/2} \end{aligned} \qquad (4)$$

$$a_{21} = [(P_1/P_2)_{t_1}(P_2/P_1)_{t_2}(A_0/B_0)^3 \exp(-A_0 - B_0)]^{1/2} \qquad (5)$$

where $(P_1/P_2)_{t_1}$ is the ratio of the vapor pressures of the two pure components at the boiling point $t_1(T_1)$ of component 1 and $(P_1/P_2)_{t_2}$ is that at the boiling point $t_2(T_2)$ of component 2. A_0 and B_0 are constants. In general organic solution tends to be ideal with increase of temperature (*1*), so that the following temperature dependence of constants A_0 and B_0 are assumed empirically:

$$A'_0 = A_0\,(T_1/T'_1)^n \qquad (6a)$$

$$B'_0 = B_0\,(T_2/T'_2)^n \qquad (6b)$$

where A_0 and B_0 without primes refer to the known data of a system and those with primes to those to be predicted under different pressure of the same system. The exponent n is an arbitrary constant.

Now before an actual calculation is made some proper assignment must be made for the numerical value of the exponent n. Equations (2) to (5) were derived by combining Equation (1) and the Van Laar equations at the limiting concentrations ($x_1 \rightarrow 1$ and $x_2 \rightarrow 1$). In accordance with the regular solution theory (*8*) the activity coefficients of components 1 and 2 in a binary solution in terms of the properties of the pure constituents are given by

$$\ln \gamma_1 = (V_1/RT)Z_2^2\,(\delta_1 - \delta_2)^2 \qquad (7a)$$

$$\ln \gamma_2 = (V_2/RT)Z_1^2\,(\delta_1 - \delta_2)^2 \qquad (7b)$$

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TABLE 1. BASIC DATA FOR PREDICTION

System	Total press., mm. Hg	2, a_{12}	a_{21}/a_0	A_0	B_0	$\left(\frac{P_1}{P_2}\right)_{t_1}$	$\left(\frac{P_1}{P_2}\right)_{t_2}$	t_1, °C.	t_2, °C.
1. *n*-heptane-ethylbenzene* (*12*)	760	2.10	0.294	0.394	0.261	3.12	2.62	98.4	136.2
2. *n*-hexane-toluene* (*12*)	760	2.54	0.221	0.432	0.360	3.914	3.157	68.7	110.6
3. Methylcyclohexane-toluene* (*15*)	760	1.05	0.625	0.236	0.205	1.330	1.303	100.9	110.6
4. Naphthalene-tetradecane† (*7*)	760	1.494	0.424	0.465	0.117	2.38	2.10	217.9	252.5
5. *n*-octane-ethylbenzene* (*18*)	760	1.11	0.60	0.201	0.227	1.338	1.328	125.7	136.2
6. 2, 2, 4-trimethyl pentane-toluene* (*4*)	760	1.028	0.585	0.309	0.225	1.400	1.364	99.2	110.6
7. Water-diacetone alcohol** (*5*)	400	1.426	0.0374	2.065	1.198	11.242	8.067	83.0	146.3

* The vapor pressure data for these systems were calculated by the use of the Antoine equation (*9*).
† The vapor pressures were taken from Stull (*16*).
** The vapor pressures of diacetonealcohol were taken from the same source as vapor-liquid equilibrium data, and the vapor pressures of water were obtained from Lange (*9*).

The usual Van Laar equations are obtained by the following substitution

$$A = (V_1/RT)(\delta_1 - \delta_2)^2 \qquad (8a)$$

$$B = (V_2/RT)(\delta_1 - \delta_2)^2 \qquad (8b)$$

Recently Cornelissen and Waterman (*3*) have found that when the vapor pressures of the pure hydrocarbons are plotted against $T^{-1.5}$ with semilog scale, a straight line is obtained. From this relation the Clausius-Clapeyron equation suggests that the heats of vaporization of hydrocarbons are proportional to $T^{-0.5}$. When one assumes that the temperature dependence of the energy of vaporization is approximately the same as that of heat of vaporization, the temperature dependence of A of Equation (8*a*) is expressed as follows:

$$\begin{aligned} A &= (V_1/RT)(\delta_1 - \delta_2)^2 \\ &= (V_1/RT)[(\Delta E/V)_1^{1/2} - (\Delta E/V)_2^{1/2}]^2 = (V_1/RT) \\ &\quad [(k/T^{1/2}V)_1^{1/2} - (k/T^{1/2}V)_2^{1/2}]^2 \\ &= (1/RT^{1.5})[k_1^{1/2} - (k_2 V_1/V_2)^{1/2}]^2 \end{aligned} \qquad (9)$$

Since the ratio of the molar volumes of the components cannot be changed so much with rise in temperature, and since the same holds for B of Equation (8*b*), it is found that the constants A and B [consequently A_0 and B_0 in Equations (2) to (5)] are proportional to $T^{-1.5}$. Thus the numerical value of n is 1.5 for organic solution and zero for aqueous solution. Lu stressed the pressure dependence of constants A_0 and B_0. In this paper the stress is laid on the temperature dependence of them.

RESULTS

The present method is tested for six hydrocarbon systems under twenty-one different pressures and one aqueous systems under four pressures. All of these systems show a considerable deviation from ideality. The vapor-pressure data for the pure components were taken from Lange (*9*), Stull (*16*), and the same sources as those of the *x-y* data. The primary information needed for prediction was obtained from the *x-y* data at atmospheric pressure or some pressure close to atmospheric and is listed in Table 1. The constants used for prediction and the predicted results are given in Table 2. On Column 9 in Table 2 the symbol $|y_{pred} - y_{expt}|_{avg}$ represents the average deviation of the predicted values from the smoothed experimental data at nine points at the interval of 0.1 mole fraction. The sign $|\ \ |$ means an absolute value. Comparing the results of Lu's method with those of the present work one notices that the average deviation of all results from the experimental data is 0.007 by the former and 0.005 by the latter. The calculated results for the *n*-heptane-ethylbenzene and water-diacetone alcohol systems are compared with the data of Myers (*12*) and Hack and Van Winkle (*5*) in Figures 1 and 2, respectively.

NOTATION

a_{12}, a_0 a_{21} = constants of Prahl's equation
A, B = constants of Van Laar equations
A_0, B_0 = constants of a given system

TABLE 2. PREDICTED CONSTANTS AT VARIOUS PRESSURES

System	Total press., mm. Hg	a_{12}	a_{21}	a_0	$\left(\frac{P_1}{P_2}\right)_{t_1}$	$\left(\frac{P_1}{P_2}\right)_{t_2}$	t_1, °C.	t_2, °C.	$\lvert y_{pred} - y_{expt}\rvert_{avg}$ Lu	This work
1. *n*-heptane-ethylbenzene (*12*)	100	2.535	1.348	6.606	4.21	3.51	41.8	74.1	0.010	0.003
	300	2.299	1.401	5.714	3.59	3.04	69.7	104.7	0.009	0.004
2. *n*-hexane-toluene (*12*)	150	3.133	0.922	5.928	5.330	4.061	24.8	61.9	0.006	0.005
	300	2.854	0.945	5.190	4.651	3.655	41.9	80.9	0.008	0.004
3. Methylcyclohexane-toluene (*17*)	200	1.103	0.970	1.753	1.462	1.425	59.6	69.5	0.008	0.005
	400	1.072	0.988	1.680	1.388	1.361	79.7	89.5	0.007	0.005
4. Naphthalene-tetradecane (*7*)	50	2.100	6.329	22.072	3.97	2.98	124.9	158.5	0.005	0.005
	100	1.860	6.100	19.785	3.36	2.80	145.5	178.5	0.007	0.005
	200	1.703	6.108	17.988	2.94	2.57	167.7	201.8	0.006	0.004
	400	1.588	6.122	16.250	2.62	2.34	193.2	226.8	0.003	0.003
5. *n*-octane-ethylbenzene (*18*)	50	1.090	0.625	1.210	1.437	1.424	49.8	57.7	0.008	0.008
	200	1.094	0.649	1.168	1.388	1.375	83.6	92.7	0.007	0.005
	500	1.097	0.666	1.138	1.356	1.344	111.2	121.3	0.004	0.003
	atm.									
6. 2, 2, 4-trimethyl pentane-toluene (*4*)	2.02	1.002	1.271	2.021	1.324	1.298	126.2	137.4	0.008	0.008
	4.06	0.978	1.299	1.924	1.254	1.235	157.9	168.6	0.007	0.007
	mm. Hg									
7. Water-diacetone alcohol (*5*)	50	1.975	0.636	20.570	15.560	10.757	38.1	90.6		0.004
	100	1.725	0.643	17.720	13.603	9.831	51.6	107.4		0.007
	200	1.560	0.620	16.627	12.292	8.938	66.4	125.9		0.006

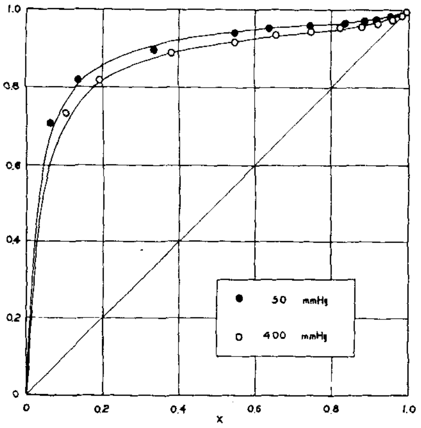

Fig. 2. Predicted and experimental vapor-liquid equilibrium for water-diacetone alcohol system (5): ——— predicted, o experimental.

A'_0, B'_0 = predicted values of A_0 and B_0
ΔE = internal energy of vaporization
k = constant
n = exponent
P = vapor pressure of pure component
R = gas constant
t = temperature, °C.
T = temperature, °K.
V = molar volume
x = mole fraction in liquid phase
y = mole fraction in vapor phase
Z = volume fraction
γ = activity coefficient
δ = solubility parameter of Hildebrand (8)

Subscripts

1, 2 = components 1 and 2 Hildebrand (8)

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Part II. Hydrocarbon Systems

This article proposes an empirical method for predicting the vapor-liquid equilibrium data on binary hydrocarbon systems without any experimental data on the mixtures. The method was tested for twenty-six systems under atmospheric pressure and three isothermal systems. The predicted results are in excellent agreement with experimental data.

The increasing importance of obtaining accurate and complete vapor-liquid equilibrium data on nonideal mixtures for the design of distillation equipments in chemical industries stimulates one to devote his efforts to accumulating new data and correlating them. However existing literature data are now sketchy, so that available methods are useful for extending a limited amount of boiling point data, azeotropic data, or solubility data into prediction of vapor-liquid equilibria over the entire concentration range with a sufficient degree of accuracy and also for extending vapor-liquid equilibrium data available at a given condition (temperature or pressure) to other conditions. Such methods need at least a minimum amount of data on the mixture under consideration.

The extent of deviations from ideal solution is expressed by the liquid phase activity coefficients different from unity. The values of the activity coefficients are strongly dependent upon the differences in intermolecular forces, polarity, chemical structure, and molecular size among the individual components in the mixtures. Recently Pierotti, Deal, and Derr (*23*) presented a very interesting attempt to express the terminal values of activity coefficients as a function of the molecular structure of the binary components quantitatively.

Prediction of vapor-liquid equilibria of binary hydrocarbon mixtures, which show positive deviation from ideality, with the usual two-constant Margules or Van Laar equations evaluated from such two terminal values cannot give satisfactory results, if they are applied for a system of a wide boiling range, because these equations are valid only at isothermal conditions and are not suitable for the isobaric systems (*3*, *21*). In this case one must take into consideration the temperature dependence of activity coefficients and follow a lengthy process of calculations.

A simple approach to the same problem was suggested by Lu and Graydon (*17*). They proposed an empirical method in prediction of vapor-liquid behavior for binary hydrocarbon systems containing one aromatic component using only the physical properties of pure components. Their calculated results were in good agreement with experimental data on fourteen systems at atmospheric pressure with three notable exceptions: benzene-2,4-dimethyl pentane, benzene-2,2,3-trimethyl butane, and *n*-pentane-benzene systems. The present article presents a modification of Lu-Graydon's method to include paraffin-naphthene mixtures. Not only isobaric systems but also isothermal systems can be treated by this method as well.

PROPOSED METHOD

A_0 and B_0 in Equations (2) to (5) of Part I are empirically expressed in the same form as proposed by Lu and Graydon. Thus

$$A_0 = \frac{1}{E}\left|\delta_1 - (\delta_1\delta_2)^{1/2}\right| (C_1 + C_2) \quad \text{at } t_1 \qquad (1)$$

$$B_0 = \frac{1}{E}\left|\delta_2 - (\delta_1\delta_2)^{1/2}\right| (C_1 + C_2) \quad \text{at } t_2 \qquad (2)$$

where δ is the solubility parameter of Hildebrand (*11*). The quantities C_1 and C_2 are constants defined below, which differ from the definition by Lu and Graydon in its temperature factor.