VAPOR-LIQUID EQUILIBRIUM RELATIONS PREDICTED BY THERMODYNAMIC EXAMINATION OF ACTIVITY COEFFICIENTS

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Data on vapor-liquid equilibria are of considerable importance from a theoretical point of view and from the standpoint of industry. For ideal solutions these data can be readily calculated, but unfortunately most solutions are nonideal in behavior. Although many data are available on nonideal solutions, there is no way, in the absence of experimental data, at present to predict quantitatively the deviations from nonideality.

It is possible to define thermodynamically certain functions, such as activity coefficients, which measure the degree of departure from ideality. The ideal situation would be one in which these activity coefficients could be predicted from properties of the pure components of the solution. Such a prediction, however, would have to be consistent with rigorous thermodynamic relations. The most promising concentration range in which to work, if the activity coefficients are to be related to the properties of pure compounds, is the dilute region. In this study most attention has been paid to collection of data and to thermodynamic analysis in this region. Work is described which, it is felt, contributes to the solution of the problem of prediction of activity coefficients, and the way is pointed for future work.

A discussion of the fundamental concept of activity coefficients and other thermodynamic quantities will be helpful in making this analysis. Also, an understanding of activity coefficients at infinite dilution will be important in developing a method of correlation of these coefficients for binary systems.

FUGACITY, ACTIVITY, ACTIVITY COEFFICIENT

Activity is defined as the ratio of the fugacity of a component in a given state to the fugacity of the pure component in some arbitrarily chosen standard state at the same temperature T. The given state may be taken as the component in solution, and the standard state as the pure component at the temperature and pressure of the solution. Thus the activity expresses the variation of fugacity with composition and for nonideal solutions shows the deviation from ideality. This deviation is more clearly expressed by activity coefficients, the ratio of the activity of one component to the mole fraction of that component in solution. For ideal solutions this ratio equals unity. In nonideal solutions the ratio becomes some value other than unity, expressing the deviation from ideality.

For liquid solutions the activity coefficient may be expressed by

$$\gamma_1 = \frac{(f_1)_L}{x_1\,(f_1^\circ)_L} \tag{1}$$

where subscript L designates the liquid state, $x_1 =$ mole fraction of component 1 in the liquid, and $(f_1^\circ)_L =$ fugacity of pure component 1 as a liquid at the temperature and pressure of the solution. at low pressures

$$(f_1^\circ)_L = \overset{*}{P_1} \tag{2}$$

where $P_1^* =$ vapor pressure of pure component 1 at the temperature of the solution.

At equilibrium, assuming fugacity rule holds for the vapors,

$$(f_1)_L = (f_1)_V = y_1\,(f_1^\circ)_V \tag{3}$$

where subscript V designates the vapor state, $y_1 =$ mole fraction of component 1 in the vapor, and $(f_1^\circ)_V =$ fugacity of pure component 1 as a vapor at the temperature and pressure of the solution.

At low pressures and temperatures, such that the fugacity coefficient equals unity,

$$(f_1^\circ)_V = \pi \tag{4}$$

and

$$(f_1)_V = y_1\pi = p_1 \tag{5}$$

where $\pi =$ total pressure on the system and $p_1 =$ partial pressure of component 1 in the vapor.

Under these conditions Equation (1) reduces to

$$\gamma_1 = \frac{p_1}{x_1\,\overset{*}{P_1}} = \frac{y_1\pi}{x_1\,\overset{*}{P_1}} \tag{6}$$

The ratio y/x is the equilibrium vaporization constant, K, and an expression for this constant may be derived in terms of activity coefficients.

$$\frac{y_1}{x_1} = K_1 = \frac{\gamma_1\,\overset{*}{P_1}}{\pi} \tag{7}$$

For high pressures the relationship becomes

$$\frac{y_1}{x_1} = K_1 = \frac{\gamma_1\,(f_1^\circ)_L}{(f_1^\circ)_V} \tag{8}$$

Equation (8) is the more exact expression, although Equation (7) may be used where the ideal-gas law and the fugacity rule for the gas phase are applicable. For ideal solutions, that is, when the activity coefficient is unity, the equilibrium constant becomes equal to the ratio of the fugacity of the pure component in the liquids to that in the vapor.

$$K_1^* = \frac{(f_1^\circ)^*_L}{(f_1^\circ)^*_V} \tag{9}$$

where the superscript* designates the ideal-solution condition.

For a given nonideal solution there are two equilibrium vaporization constants which may be evaluated: one for the nonideal system and one for the same system considered as an ideal system. The symbol K^* will indicate the ideal-equilibrium vaporization constant. An expression for activity coefficient may now be written in terms of K and K^*.

$$\gamma_1 = K_1/K_1^* \tag{10}$$

For nonideal solutions

$$\gamma_1 (f_1^\circ)_L = (f_1)_L / x_1 \qquad (11)$$

For ideal solutions

$$(f_1^\circ)^*_L = (f_1)^*_L / x_1 \qquad (12)$$

Combining Equations (8) through (12) gives

$$\gamma_1 = \frac{K_1}{K_1^*} = \frac{(f_1)_L/(f_1^\circ)_V}{(f_1)^*_L/(f_1^\circ)^*_V} \qquad (13)$$

At very low concentrations such that the boiling point of the nonideal solution approaches that of the ideal solution

$$(f_1^\circ)_V = (f_1^\circ)^*_V \qquad (14)$$

Equation (13) now becomes

$$\gamma_1 = \frac{K_1}{K_1^*} = \frac{(f_1)_L}{(f_1)^*_L} \qquad (15)$$

If the temperature and pressure are so low that the fugacity coefficients are equal to unity, Equation (15) may be written as

$$\gamma_1 = \frac{K_1}{K_1^*} = \frac{P_1}{P_1^*} \qquad (16)$$

where $P_1 = p_1/x_1 =$ "nonideal" vapor pressure of *pure* component 1. $P_1^* =$ "ideal" vapor pressure of pure component 1, or the actual vapor pressure of pure component 1 at the temperature of the solution.

The assumptions involved in Equation (16) restated are (1) that the temperature and pressure of the solution are so low that the fugacity coefficients are substantially equal to unity, (2) that the concentrations of the solution are so dilute that the differences in boiling points of the ideal and nonideal solutions are negligible, and (3) that the total pressures of the solutions are equal. Similar expressions may be written for component 2 expressing the nonideal vapor pressure of this component. These nonideal vapor pressures will be useful in correlating the activity coefficients at infinite dilution for different systems.

ACTIVITY COEFFICIENTS AT INFINITE DILUTION

Carlson and Colburn *(4)* suggest a method for finding the deviations from Raoult's law for systems composed of a member of a homologous series of compounds and another compound. This method is based on equations derived by Scatchard *(12)* for systems in which the change of entropy on mixing is the same as that for an ideal mixture. This assumption is not justified in many cases of nonideal solutions.

Another method of handling the activity coefficients of the components in dilute solution has been to relate them to the constants in equations such as the van Laar equations given by Carlson and Colburn in the following forms:

$$\log \gamma_1 = \frac{A x_2^2}{[(A/B)x_1 + x_2]^2} \qquad (17)$$

$$\log \gamma_2 = \frac{B x_1^2}{[x_1 + (B/A)x_2]^2} \qquad (18)$$

Since A is the terminal value of $\log \gamma_1$, where $x_2 = 0$, and B is the terminal value of $\log \gamma_2$, where $x_2 = 0$, it has been suggested that these constants be obtained by plotting the logarithm of the activity coefficient against the mole fraction and extrapolating the curves to zero concentration. These extrapolations, however, are of very uncertain accuracy. Also, the van Laar equations are restricted to constant temperature, and this extrapolation is usually made from data obtained at constant pressure. The van Laar and other two-constant equations are frequently used for correlating vapor-liquid equilibrium data for nonideal solutions. The equations involve certain assumptions, and generally when one equation fails, the other two-constant equations fail.

Butler and Harrower *(3)* have considered the quantity p/x, which is called the nonideal vapor pressure in this work, and its variation in systems of homologous series of compounds and another type of compound. The free energies of solution from the vapor, $RT \ln p/x$, at a constant temperature have been related to the number of carbon atoms in compounds of the homologous series, even though the solutions showed large deviations from ideality. These free energies of solution were found to change regularly as the number of carbon atoms in the molecule was increased or decreased in the cases studied, specifically alcohols and alkyl halides in benzene, carbon tetrachloride, and cyclohexane. Use of the nonideal vapor pressure in the present work avoids an anomaly of the quantity p/x, tending to become indeterminate as the solution becomes very dilute, that is, as x approaches zero.

An understanding of the significance of activity coefficients at infinite dilution requires a recognition of certain facts concerning the familiar x-y diagram. It follows, from Equation (8), that at $x_1 = 0$

$$\left[\frac{\partial y_1}{\partial x_1}\right]_{x_1=0} = (K_1)_{x_1=0} = (\gamma_1)_{x_1=0}\left[\frac{(f_1^\circ)_L}{(f_1^\circ)_V}\right]_{x_1=0} \qquad (19)$$

Necessarily, $(f_1^\circ)_L$ and $(f_1^\circ)_V$ are evaluated at the temperature and pressure conditions existing at $x_1 = 0$, that is, the boiling point and pressure of component 2. Similarly, for component 2, at $x_2 = 0$

$$\left[\frac{\partial y_1}{\partial x_1}\right]_{x_1=1} = \left[\frac{\partial y_2}{\partial x_2}\right]_{x_2=0} = (K_2)_{x_2=0} = (\gamma_2)_{x_2=0}\left[\frac{(f_2^\circ)_L}{(f_2^\circ)_V}\right]_{x_1=0} \qquad (20)$$

Here $(f_2^\circ)_L$ and $(f_2^\circ)_V$ are the fugacities of component 2 evaluated at the boiling point and pressure of component 1. If the system were acting ideally, the activity coefficients would be unity and the slopes at infinite dilution of the ideal system would be

$$(\partial y_1/\partial x_1)^*_{x_1=0} = (K_1^*)_{x_1=0} = \left[\frac{(f_1^\circ)_L}{(f_1^\circ)_V}\right]_{x_1=0} \qquad (21)$$

$$(\partial y_1/\partial x_1)^*_{x_1=1} = (K_2^*)_{x_2=0} = \left[\frac{(f_2^\circ)_L}{(f_2^\circ)_V}\right]_{x_1=1} \qquad (22)$$

If Equation (19) is divided by Equation (21), a relationship is obtained which expresses the activity coefficient at infinite dilution. This points out the fact that the nonideality of a system is indicated by the deviation of the slope of the x-y diagram at infinite dilution from the slope for the same system acting ideally.

At low pressures and temperatures, $(f_1^\circ)_L$ becomes P_1^* and $(f_1^\circ)_V$ becomes π. The slopes at infinite dilution of the x-y diagram for the nonideal system and for the ideal system become

TABLE 1.—TYPICAL EXPERIMENTAL RESULTS, VAPOR-LIQUID EQUILIBRIUM DATA

System: benzene-ethanol

x_1	y_1	Temp., °C.	Pressure, mm. Hg	γ_1	γ_2	$\ln\gamma_1$	$\ln\gamma_2$
0.0000	0.0000	80.10	760.5	10.48*	1.0007	2.350*	0.00070
0.0048	0.0400	78.60	760.0	8.2427	1.0128	2.10933	0.01272
0.0085	0.0790	77.11	760.5	9.7542	1.0219	2.27770	0.02166
0.1720	0.3560	68.90	760.0	3.0351	1.1219	1.11024	0.11502
0.3085	0.4040	67.98	760.0	1.9898	1.2789	0.68803	0.24600
0.4855	0.4490	67.67	760.0	1.4230	1.6051	0.35277	0.47319
0.7545	0.5720	69.18	760.0	1.0956	2.4838	0.09130	0.90979
0.8815	0.7030	71.86	760.0	1.0324	3.2668	0.03189	1.18381
0.9870	0.9545	77.51	760.0	0.9983	3.7125	−.00170	1.31171
0.9910	0.9685	77.75	760.0	0.9994	3.6771	−.00060	1.30212
1.0000	1.0000	78.32	760.3	1.0004	3.568*	0.00040	1.272*

Component 1 is ethanol; *extrapolated values.

TABLE 2.—TYPICAL EXPERIMENTAL RESULTS, VAPOR-LIQUID EQUILIBRIUM DATA

System: benzene–*n*–propanol

x_1	y_1	Temp., °C.	Pressure, mm. Hg	γ_1	γ_2	$\ln\gamma_1$	$\ln\gamma_2$
0.0000	0.0000	80.10	759.7	5.165*	0.9996	1.642*	−.0004
0.0270	0.0590	79.23	759.7	4.5723	0.9935	1.52002	−.0065
0.0445	0.0870	78.68	760.0	4.1908	0.9849	1.43298	−.0150
0.0980	0.1475	77.69	759.7	3.2813	1.0196	1.18824	0.01941
0.2300	0.2170	77.21	760.0	2.1561	1.1440	0.76830	0.13453
0.5015	0.3075	78.19	760.0	1.3426	1.4756	0.29461	0.38907
0.6725	0.3900	81.10	760.3	1.1206	1.8059	0.11386	0.59106
0.8540	0.5705	86.50	760.3	1.0285	2.4157	0.02811	0.88199
0.9375	0.7490	91.39	761.5	1.0086	2.8538	0.00857	1.04865
0.9560	0.8060	92.29	760.3	1.0249	3.0464	0.02459	1.11396
0.9730	0.8640	94.11	760.3	1.0037	3.3003	0.00370	1.19401
0.9760	0.8775	94.23	760.3	1.0114	3.3325	0.01134	1.20372
0.9800	0.8830	94.37	760.3	1.0080	3.8041	0.00797	1.33608
0.9885	0.9380	95.70	760.0	1.0067	3.3690	0.00668	1.21462
1.0000	1.0000	97.20	760.0	1.0003	4.031*	0.00030	1.394*

Component 1 is *n*-propanol; *extrapolated values.

$$(\partial y_1/\partial x_1)_{x_1=0} = (\overset{*}{P_1}/\pi)_{x_1=0}$$

$$(\gamma_1)_{x_1=0} = (P_1/\pi)_{x_1=0} \quad (23)$$

$$(\partial y_1/\partial x_1)^{*}_{x_1=0} = (\overset{*}{P_1}/\pi)_{x_1=0} \quad (24)$$

Consider the conditions existing at the point $x_2 = 0$ in a series of systems such as the benzene-alcohol series. Here the subscript 1 indicates the alcohol and 2, the benzene. At constant total pressure π, the temperature of the solution at $x_2 = 0$ will be the boiling point of the alcohol. The ideal slopes of the *x-y* diagram of the solutions of the various alcohols in benzene will vary as the vapor pressure of benzene varies with temperature. This follows from Equation (24) written in terms of component 2. This variation will be a straight line on a log P_2^* vs. $1/T$ plot, where P_2^* is the vapor pressure of pure benzene and T is the absolute temperature. This suggests a method of correlating the nonideal slopes, that is, by plotting the logarithm of the nonideal slope vs. the reciprocal of the absolute temperature. This nonideal slope is proportional to the nonideal vapor pressure of the pure component as shown in Equation (23).

At the point $x_1 = 0$ the conditions at constant total pressure are similar to those described above with one important difference. The temperature is constant at the boiling point of benzene, component 2, and the ideal slopes for the different systems now vary as the vapor pressures of the different alcohols at this constant temperature. The vapor pressure of the methanol at this temperature is higher than that of ethanol, of *n*-propanol, and of other higher alcohols in the series. It is possible to relate the ideal vapor pressures of these different compounds by use of the boiling points; therefore, slopes $(\partial y_1/\partial x_1)^*_{x_1=0}$ can be related to temperature for the different systems. A plot of log P_1^* vs. $1/T$ is usually satisfactory and this suggests that a similar correlation for the nonideal vapor pressure and therefore, the nonideal slopes, should be used.

The net result of these correlations as presented above may be shown mathematically as follows:

$$\log (P_1/\pi)_{x_1=0} = (M/T) + N \quad (25)$$

$$\log (P_1^*/\pi)_{x_1=0} = (M^*/T) + N^* \quad (26)$$

where M, N, M^*, and N^* are constants and T is the absolute temperature. By subtraction

$$\log (P_1/P_1^*)_{x_1=0} = (M - M^*)/T + (N - N^*) \quad (27)$$

Since by Equation (19)

$$(\gamma_1)_{x_1=0} = (P_1/P_1^*)_{x_1=0} \quad (28)$$

$$\log (\gamma_1)_{x_1=0} = (A'/T) \times B' \quad (29)$$

Similarly,

$$\log (\gamma_2)_{x_2=0} = (A''/T) + B'' \quad (30)$$

where $T =$ absolute temperature. Equations (25) and (26) permit estimation of $(\partial y_1/\partial x_1)_{x_1=0}$ and $(\partial y_1/\partial x_1)_{x_1=1}$ for higher alcohols in the series by extrapolation, provided these slopes are known for lower members in the series. From these nonideal slopes, activity coefficients at infinite dilution may be calculated and used in equations such as those of van Laar for determining the vapor-liquid equilibria of the system.

CALCULATION PROCEDURE

By use of the data in Tables 1 and 2, which were collected on benzene-ethanol and benzene–*n*-propanol, and those of Gautreaux

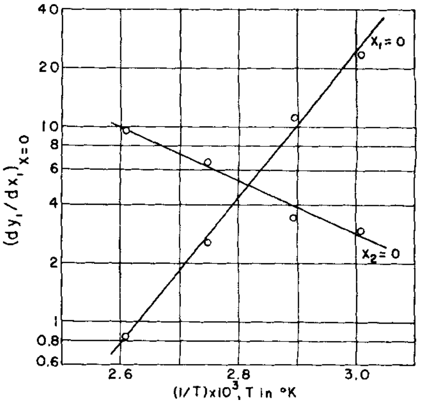

FIG. 1. NONIDEAL SLOPE OF *x-y* DIAGRAM VS. $1/T$ BENZENE ALCOHOLS.

(*6*) on benzene-methanol the *x-y* diagrams were constructed and the initial slopes $\partial y/\partial x$ were determined. These are tabulated in Table 3 and plotted in Figure 1 vs. the reciprocal of the absolute temperature. A straight line resulted. The lines were extended to the benzene-butanol range and extrapolated values of the slopes $\partial y/\partial x$ for this system were read. Later data were collected on the benzene-butanol system and compared with the predicted results obtained by the method shown below.

An example of this type of calculation, for the benzene–*n*-butanol system, follows. The Van Laar equations are used in this example but any two-constant equation might be used.

At $T = 117.50°\text{C.} = 390.50°\text{K.}$ the normal boiling point of *n*-butanol $1/T = 0.002560/°\text{K.}$

$$(\partial y_1/\partial x_1)_{x_1=0} = 0.840, \text{ from Figure 1}$$

$$(\partial y_1/\partial x_1)_{x_2=0} = 9.70, \text{ from Figure 1}$$

$$(\partial y_1/\partial x_1)^*_{x_1=0} = \frac{(f_1^o)_L}{(f_1^o)_V} =$$

$$\frac{(v P_1^*)\; P_1^*\, e^{V_1\,(\pi - P_1)/RT}}{(v_\pi)_1\, \pi} =$$

0.2189 (at boiling point of benzene)

$$(\partial y_1/\partial x_1)^*_{x_2=0} = \frac{(f_2^o)_L}{(f_2^o)_V} =$$

$$\frac{(\bar{v} P_2^*)\; P_2^*\, e^{V_2\,(\pi - P_2)/RT}}{(v_\pi)_2\, \pi} =$$

2.7752 (at boiling point of *n*-butanol)

$$(\gamma_1)_{x_1=0} = 0.840/0.2189 = 3.837$$

$$(\gamma_2)_{x_2=0} = 9.70/2.7752 = 3.495$$

$$A = \log(\gamma_1)_{x_1=0} = \log 3.837 = 0.58399$$

$$B = \log(\gamma_2)_{x_2=0} = \log 3.495 = 0.54345$$

Activity coefficients over the entire concentration range may be determined by substitution in the van Laar equations (*4*).

The following procedure permits calculation of *x* and *y* from the activity coefficients (*8*).

1. Assume a boiling point for the solution of composition x_1.
2. Determine P_1^* and P_2^* at this temperature.
3. Calculate *y* by the following equation:

$$y_1 = \frac{x_1\, P_1^*\, \gamma_1}{x_1\, P_1^* + x_2\, P_2^*\, \gamma_2}$$

4. Check the assumed temperature by calculating P_1^*:

$$P_1^* = \frac{y_1 \pi}{\gamma_1\, x_1}$$

This procedure is repeated until a satisfactory check is obtained. The second assumption usually provides an adequate check.

Figure 2 shows a plot which was prepared for the system benzene–*n*-butanol by this procedure. Experimental points collected on this same system are also shown, and the agreement is good. Bonauguri et al. (*2*) report data, collected at 740 mm., which is in general agreement with these data when allowance for the difference in pressure is made. Similar calculations were made on the system benzene–*n*-amyl alcohol and good agreement was obtained between the calculated and experimental results.

EXPERIMENTAL METHODS

The reagents used were benzene, ethyl alcohol, *n*-propyl alcohol, *n*-butyl alcohol and *n*-amyl alcohol.

The benzene was purchased from Merck and Company and purified by redistillation. The fraction used in this work had a refractive index n_D^{25} of 1.4979, in agreement with values reported in International Critical Tables (*14*). The ethanol was purchased from U. S. Industrial Chemicals, the *n*-propanol from Fisher Scientific Company. Both of these were treated with magnesium by the method of Fieser (*5*) to remove any water present. The refractive index n_D^{25} of the purified ethanol was 1.3595, compared with literature values (*12*) of 1.3594 to 1.3596; that of *n*-propanol was 1.3938, compared with literature values (*9*) of 1.3834.

The *n*-butanol and *n*-amyl alcohols were obtained from the Fisher Scientific Company. These were purified by redistillation in an Oldershaw column. The purified *n*-butanol had a refractive index n_D^{25} of 1.3992, compared with a literature value (*7*) of 1.3993; the purified *n*-amyl alcohol had a refractive index n_D^{25} of 1.4082, compared with a literature value (*13*) of 1.4084.

Densities were also determined and good agreement was obtained with literature values. Refractive indices were determined with a Bausch and Lomb precision refractometer, model 33-45-01.

TABLE 3.—SLOPE AT INFINITE DILUTION OF *x-y* DIAGRAMS FOR BENZENE-ALCOHOL SYSTEMS

System	$\left(\frac{\partial y_1}{\partial x_1}\right)^*_{x_1=0}$	$\left(\frac{\partial y_1}{\partial x_1}\right)_{x_1=0}$	$(\gamma_1)_{x_1=0}$	T, °K.
Benzene-methanol	1.7808	23.605	13.255	337.9
Benzene-ethanol	1.0677	11.189	10.48	351.5
Benzene–*n*-propanol	0.5008	2.587	5.165	370.4
Benzene–*n*-butanol	0.2189	0.840†	3.837	390.7

System	$\left(\frac{\partial y_1}{\partial x_1}\right)^*_{x_2=0}$	$\left(\frac{\partial y_1}{\partial x_1}\right)_{x_2=0}$	$(\gamma_2)_{x_2=0}$	T, °K.
Benzene-methanol	0.6099	2.9551	4.845	337.9
Benzene-ethanol	0.9684	3.4552	3.568	351.5
Benzene–*n*-propanol	1.6400	6.6108	4.031	370.4
Benzene–*n*-butanol	2.7752	9.70†	3.495	390.7

The values of $(\partial y_1/\partial x_1)_{x=0}$ were obtained by calculation from $(\gamma)_{x=0}$ and $(\partial y_1/\partial x_1)^*_{x=0}$.

†Extrapolated values.

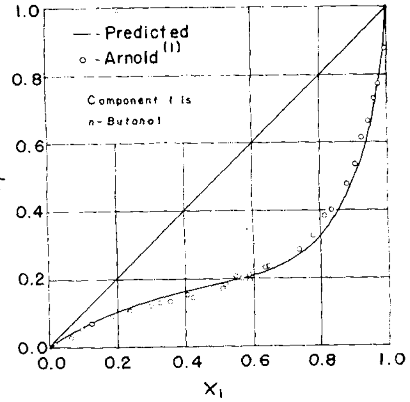

FIG. 2. *x-y* DIAGRAM FOR BENZENE–*n*-BUTANOL; PRESSURE: 760 MM. HG.

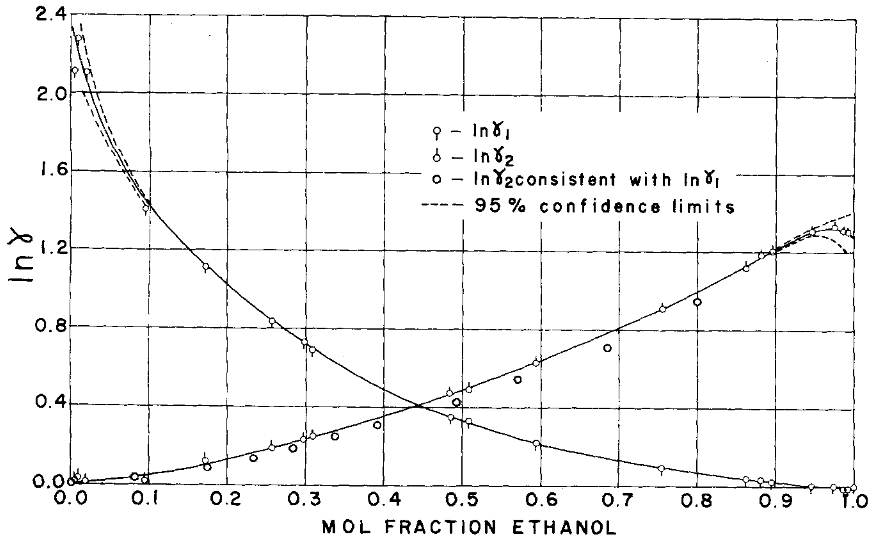

Fig. 3. Logarithm Activity Coefficient vs. Mole Fraction Ethanol, Benzene-Ethanol System.

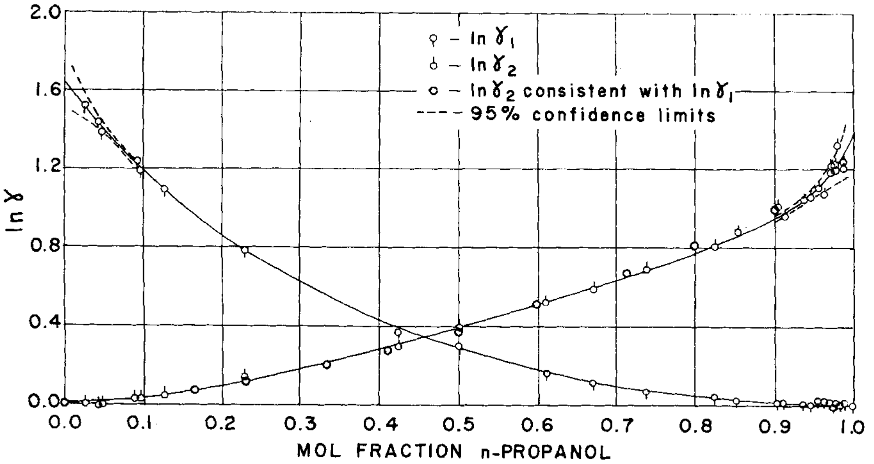

Fig. 4. Logarithm Activity Coefficient vs. Mole Fraction *n*-Propanol, Benzene–*n*-Propanol System.

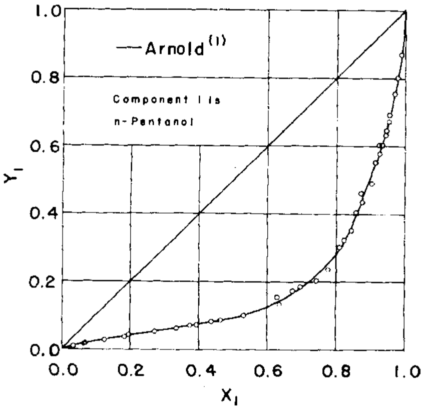

Fig. 5. *x-y* Diagram for Benzene–*n*-Pentanol; Pressure: 760 mm. Hg.

APPARATUS AND PROCEDURE

The apparatus used in collecting the present data was an equilibrium still designed by Jones, Schoenborn, and Colburn(*10*). The still had a capacity of about 65 ml. The contents of the still were protected at all times from atmospheric moisture by means of a silica gel drying tube.

Copper - constantan thermocouples were used to measure the temperatures, with an insulated ice bath to maintain a constant reference temperature. A Leeds and Northrup type *K* potentiometer capable of measuring voltages of 0.001 mv. was used to measure the thermocouple e.m.f. The null point was indicated by a suspended-coil D'Arsonval-type galvanometer, with which a bracket 0.004 mv. wide could be obtained around the correct e.m.f. reading. This is equivalent to a bracket of 0.09°C. around the correct temperature over the temperature range of these experiments.

A Cartesian-type manostat was used to regulate the pressure in the still to 760 mm. Hg and to keep pressure fluctuations to within ±2 mm. of water or ±0.1474 mm. Hg. The difference between atmospheric pressure and the still pressure was indicated by a differential water manometer. The slight vacuum was maintained by means of an aspirator.

Atmospheric pressure was measured with a mercury barometer which could be read to the nearest 0.01 Hg or 0.3 mm. Hg. Thus, any temperature fluctuations due to the variation of pressure from 760 mm. Hg were small and could be assumed negligible.

The condensed vapor and liquid samples were analyzed for composition with a Bausch and Lomb refractometer. With this instrument the refractive index could be read to the nearest 0.0001 and estimated to the nearest 0.00001. The calibration of the instrument was checked with a test glass of known refractive index supplied with the instrument.

The temperature of the instrument was held to 25°C. ± 0.2° by means of water circulation from a constant-temperature water bath. Before any vapor-liquid equilibrium data were collected, the thermocouples were calibrated. Charts relating the composition to the refractive index were prepared for each system.

The vapor-liquid equilibrium data were collected at a total pressure of 760 mm. Hg and over the entire range of concentrations.

EXPERIMENTAL DATA[*]

The experimental results obtained by the present authors consist of vapor-liquid equilibrium data for the two binary systems, benzene-ethanol and benzene–*n*-propanol, shown in Tables 1 and 2. In addition, the results of Gautreaux(*6*) on benzene-methanol and of Arnold(*1*), on benzene–*n*-butanol, and benzene–*n*-amyl alcohol have been included. These men worked on this same general project in the same laboratories as the authors.

Activity coefficients (*see* Figures 3 and 4) for component 2, which are thermodynamically consistent with activity coefficients for component 1, have been calculated by the Gibbs-Duhem equation to show the consistency of the data. Ninety-five per cent confidence limits, indicated by dashed lines in the figures, were also calculated for these experimental data.

Benzene-methanol data are reported by Gautreaux(*6*) at 766.4 mm. Hg total pressure.

Temperature measurements have been corrected to a total pressure of 760.0 mm. Hg by means of approximate relationships. These tempera-

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[*] Complete tables of the author's experimental data and also those of Gautreaux (*6*) and Arnold (*1*) are on file with the Photoduplication Service, American Documentation Institute, Library of Congress, Washington 25, D. C., as document 4561 and may be ordered for $1.25 for microfilm or photoprints.

ture corrections were between 0.2 and 0.3°C.

DISCUSSION OF RESULTS

The suggested method for correlation of activity coefficients has been applied to the benzene–*n*-butanol system, the results being plotted in Figure 2. It is pointed out that these vapor-liquid equilibrium data were calculated on the nonideal system benzene–*n*-butanol without the aid of any experimental data on this system.

The results of this calculation are considered to be good. Reference to Figure 2 shows that the greatest disagreement between the calculated and experimental data is between the liquid concentration ranges of 0.2 to 0.8 mole fraction. In this range the predicted line is somewhat higher than the experimental points between 0.2 and 0.5 mole fraction and is somewhat lower than the experimental points between 0.5 and 0.8 mole fraction in the liquid. The difference between the experimental and predicted values are rather small over the entire range. Similar results were obtained when this method was tried on the benzene–*n*-amyl-alcohol system.

An examination of Figure 2 shows that the calculated and experimental curves agree closely in the dilute regions, and it is therefore seen that the calculated and experimental nonideal slopes in the x-y diagram at infinite dilution also agree closely. This is evidence that the proposed correlations of these slopes at infinite dilution is reasonably satisfactory and that the differences between the calculated and experimental curves in Figure 2 are not caused by an inadequacy of the proposed correlation.

The van Laar equations were used in the example presented in this paper. One reason for the difference between the predicted and experimental data may lie in inadequacies in this equation, as has been previously mentioned. It should be borne in mind that the present method allows the prediction of the constants in any two-constant equation for activity coefficients and that the use of the van Laar equations, as such, is not part of the method. Another two-constant equation could have been used. If a three-constant equation for activity coefficients is considered necessary, then the present method should be useful in the prediction of two of the constants.

SUMMARY

The concept of the nonideal vapor pressure of a component in dilute solution has been developed and explained, and the relation between the nonideal vapor pressure and the slope of the y-x equilibrium diagram has been derived. In addition, an equation relating the nonideal vapor pressure and the boiling point of the pure component is presented.

A procedure is outlined for predicting the entire y-x diagram from these nonideal vapor pressures. The 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.

Vapor-liquid equilibrium data were collected on the systems benzene-methanol, benzene-ethanol, and benzene–*n*-propanol. These were used to predict the y-x diagram for benzene–*n*-butanol, and the agreement with experimental values was found to be good. Experimental data are also presented on the system benzene–*n*-butanol and benzene–*n*-pentanol (Figure 5).

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NOTATION

f = fugacity of component in solution
f° = fugacity of pure component at the temperature and total pressure of the solution
y = mole fraction of component in the vapor
x = mole fraction of component in the liquid
π = total pressure
p = partial pressure of component in the vapor
γ = activity coefficient of component in solution
P^* = vapor pressure of pure component at the temperature of the solution
$K = y/x$ = equilibrium vaporization constant of component
P = nonideal vapor pressure of pure component, defined by Equation (16) at low pressures and concentrations
A, B = constants in the van Laar Equations (17) and (18)
T = absolute temperature, °K.
M, N = constants in Equation (25)
M^*, N^* = constants in Equation (26)
A', B' = constants in Equation (29)
A'', B'' = constants in Equation (30)
ν = fugacity coefficient—ratio of fugacity to pressure

Subscripts

V = vapor state
L = liquid state
1, 2 = component number
P^* or π = pressure at which fugacity coefficient is evaluated

Superscripts

$*$ = the ideal-solution condition

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