Subscripts

n = any tray in distillation column
$n+1$ = tray above tray n
$n-1$ = tray below tray n
w = bottoms product

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Activity Coefficients at Infinite Dilution: 2-Propanol — Water System

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Activity coefficients at infinite dilution in the liquid phase are of interest both to physical chemists and chemical engineers. Physical chemists study them because they represent a direct macroscopic measure of the degree of interaction between a molecule of one species and an environment consisting entirely of a second species. Chemical engineers are interested in them because of their utility in the prediction of vapor-liquid equilibria for use in the design of absorbers, distilling columns, and heterogeneous reactors. This paper will illustrate a method of obtaining activity coefficients at infinite dilution from the terminal slopes of binary vapor-pressure curves. It will also illustrate the use of these data to predict equilibrium vapor and liquid compositions, including azeotrope compositions, in the concentrated region. While the methods used are not new, they are not very commonly employed at present, and it is hoped that this paper will stimulate a more general realization of the utility of these techniques.

THEORETICAL BACKGROUND

Vapor-liquid equilibrium data are most frequently correlated in terms of activity coefficients. The activity coefficient of component i in a liquid phase is defined by the relation

$$\gamma_{iL} = \frac{f_{iL}}{x_i f^o_{iL}} \tag{1}$$

The standard state commonly chosen for an activity coefficient in a liquid phase is the pure liquid at the temperature and pressure of the solution. Similarly for a vapor phase

$$\gamma_{iV} = \frac{f_{iV}}{y_i f^o_{iV}} \tag{2}$$

Equation (2) implies that the standard state for an activity coefficient in a vapor phase is the pure vapor at the temperature and pressure of the solution.

Since a pure compound at a given temperature and pressure can be stable in only one phase, it is apparent that the quantities f^o_{iL} and f^o_{iV} appearing in Equations (1) and (2) will refer to fictitious states for one or more components in each of the phases. This difficulty is removed in practice by some suitable extrapolation of the properties in question into the fictitious region. The derived values of the activity coefficients are thus seen to be defined both by appropriate forms of Equations (1) and (2) and by the extrapolation method selected.

The present discussion will be confined to systems with one vapor and one liquid phase.

If a liquid and a vapor phase are at equilibrium, the expression

$$f_{iL} = f_{iV} \tag{3}$$

may be written for each of the i components. Hence from Equations (1) and (2)

$$\gamma_{iL}\, x_i\, f^o_{iL} = \gamma_{iV}\, y_i\, f^o_{iV} \tag{4}$$

for each of the i components. All of the activity coefficients are unity in any phase behaving as an ideal solution. At low pressures $f^o_{iL} = P^o_i$ (when the very small effect of total pressure on vapor pressure is neglected) and $f^o_{iV} = P$, and Equation (4) reduces to

$$\gamma_{iL}\, x_i\, P^o_i = y_i P \tag{5}$$

Ibl and Dodge (9) have derived the following equation for a binary system at constant temperature:

$$\frac{d \ln \gamma_1}{d \ln x_1} - \frac{d \ln \gamma_2}{d \ln x_2} = \frac{1}{RT}\,(V - x_1 V^o_1 - x_2 V^o_2)\,\frac{dP}{dx_1} \tag{6}$$

The term $V - x_1 V^o_1 - x_2 V^o_2$ is the volume change on mixing the pure components at the temperature and pres-

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sure of the solution to form 1 mole of solution. The equation may be applied to any homogeneous binary phase, and the volumes V, V^o_1, and V^o_2 refer to the solution, pure component 1, and pure component 2 respectively in that phase at the temperature and pressure of the solution. It is apparent that normally either V^o_1 or V^o_2 will refer to a fictitious state and must be obtained by an extrapolation process consistent with that used for the fugacity of the pure component.

Equation (6) cannot be integrated analytically, but Ljunglin and Van Ness (*14*) have presented an iterative method suitable for machine computation.

Under certain conditions the right-hand side of Equation (6) may be negligible compared with the terms of the left-hand side, and (6) may be rewritten as

$$\frac{d \ln \gamma_1}{d \ln x_1} - \frac{d \ln \gamma_2}{d \ln x_2} = 0 \tag{7}$$

Numerous partial solutions to Equation (7) have devised by either employing empirical methods or by an analysis of the statistical behavior of solutions. One of the most useful solutions is given by the Van Laar equations:

$$\ln \gamma_1 = \frac{A}{\left(1 + \frac{A x_1}{B x_2}\right)^2} \tag{8}$$

$$\ln \gamma_2 = \frac{B}{\left(1 + \frac{B x_2}{A x_1}\right)^2} \tag{9}$$

Since Equations (8) and (9) are only particular solutions of Equation (7), which is itself a restricted version of the more general Equation (6), it is not surprising that they can be used to describe only selected sets of binary behavior. Carlson and Colburn (*2*) and Robinson and Gilliland (*17*) have discussed the derivation of these and other solutions to Equation (7) and shown that they are extremely useful in correlating a considerable range of vapor-liquid equilibrium data.

The constant A in each of these equations can be shown to be

$$\lim_{x_1 \to 0} \ln \gamma_1$$

Similarly

$$B = \lim_{x_2 \to 0} \ln \gamma_2$$

Wohl (*24*) has shown that Equations (8) and (9) are particular examples of more general equations applying to both binary and ternary systems. All of his equations retain as the principal constants the logs of binary activity coefficients at infinite dilution. Severns et al. (*20*) and Kenny (*10*) have discussed application of this approach to particular ternary systems.

Although several recent papers (*3, 16, 23*) present methods for predicting activity coefficients at infinite dilution, it is desirable to have a rapid reliable means of measuring them. Various investigators (*5*) have devised approximate means of determining them from binary P vs. x curves, but Gautreaux and Coates (*7*) apparently were the first to state an exact relation between activity coefficients at infinite dilution and the terminal slopes of the vapor-pressure curves. They presented the following equations:

$$\lim_{x_1 \to 0} \frac{\gamma_{1L}}{\gamma_{1V}} = \lim_{x_1 \to 0} \frac{f^o_{1V}}{f^o_{1L}} \left[1 + \frac{(V^o_{2V} - V^o_{2L})}{RT} \left(\frac{\partial P}{\partial x_1} \right)_T \right] \tag{10}$$

$$\lim_{x_1 \to 0} \left(\frac{\partial y_1}{\partial x_1} \right)_T = \lim_{x_1 \to 0} \left[1 + \frac{V^o_{2V} - V^o_{2L}}{RT} \left(\frac{\partial P}{\partial x_1} \right)_T \right] \tag{11}$$

At low pressures Equation (10) reduces to

$$\lim_{x_1 \to 0} \gamma_{1L} = \lim_{x_1 \to 0} \frac{P}{P^o_1} \left[1 + \frac{1}{P} \left(\frac{\partial P}{\partial x_1} \right)_T \right] \tag{12}$$

These equations are for the isothermal case, but similar ones can be derived for the isobaric case and are to be found in reference 7.

Equations (10), (11), and, within the low-pressure restriction, (12) have a very wide range of applicability. They are exact for any system in which the values of

$$\lim_{x_i \to 0} \ln \gamma_i$$

are not infinite. The only known cases of infinite values of $\lim_{x_i \to 0} \ln \gamma_i$ occur in solutions of strong electrolytes. The system hydrogen chloride-water may be taken as an example (*4, 8*). For all other classes of systems Equations (10) and (11) appear to be exact, and the errors involved in using the low-pressure approximation are readily assessed.

Rearranging Equation (4) and applying it to component 1 one obtains

$$\frac{\gamma_{1L} f^o_{1L}}{\gamma_{1V} f^o_{1V}} = y_1/x_1 \tag{13}$$

It is seen that as $x_1 \to 0$, the right-hand side becomes indeterminate. Differentiating the numerator and denominator of the right-hand side and applying L'Hospital's rule one gets

$$\lim_{x_1 \to 0} \frac{\gamma_{1L} f^o_{1L}}{\gamma_{1V} f^o_{1V}} = \lim_{x_1 \to 0} \left(\frac{dy_1}{dx_1} \right) \tag{14}$$

Equation (14) shows that the terminal slope of the y_1 vs. x_1 curve is independent of the path by which the system may approach the condition ($x_1 = 0, T, P$). Thus values of $\lim_{x_1 \to 0} \frac{dy_1}{dx_1}$ derived from two curves a and b, one at a constant temperature T_a and the other at a constant pressure P_b, will be identical providing the two curves intersect at a common point ($x_1 = 0, T = T_a, P = P_b$). That is

$$\lim_{x_1 \to 0} \left(\frac{\partial y_1}{\partial x_1} \right)_{T=T_a} = \lim_{x_1 \to 0} \left(\frac{\partial y_1}{\partial x_1} \right)_{P=P_b} \tag{15}$$

and Equation (11) can be used to calculate the initial slope of an isobaric y vs. x curve from isothermal vapor-pressure data.

Ellis and Jonah (*5*) have recently published an alternative method of calculating activity coefficients at infinite dilution from the terminal slopes of the total vapor-pressure curve. They treat gas-phase imperfections in terms of second virial coefficients and offer a graphical procedure for the evaluation of the terminal slopes.

The volatility of component 2 relative to that of component 1 is defined as

$$\alpha_{2/1} = \frac{y_2 x_1}{y_1 x_2} \tag{16}$$

If the two species 1 and 2 are dissolved in a large amount of a component 3

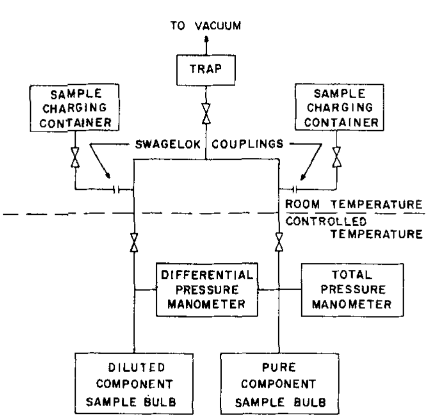

Fig. 1. Diagram of measuring system.

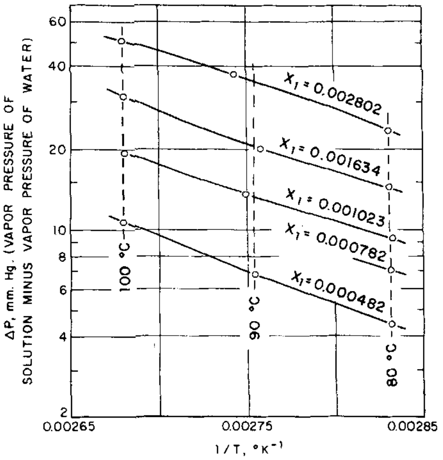

Fig. 2. Differential vapor pressure vs. temperature (water end).

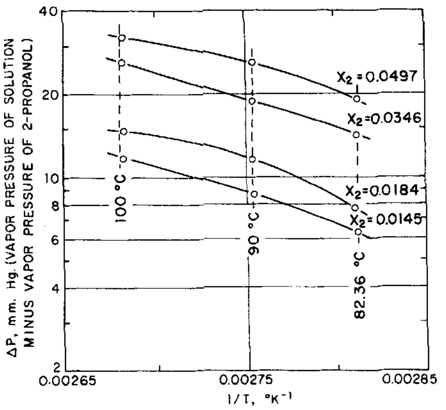

Fig. 3. Differential vapor pressure vs. temperature (2-propanol end).

$$\lim_{\substack{x_1\to 0\\ x_2\to 0\\ x_3\to 1}} \alpha_{2/1} = \lim_{\substack{x_1\to 0\\ x_2\to 0\\ x_3\to 1}} \left(\frac{\partial y_2}{\partial x_2}\right) \Big/ \left(\frac{\partial y_1}{\partial x_1}\right) \qquad (17)$$

If one writes two separate equations analogous to Equation (11) for solute species 1 and 2 at infinite dilution in a third component 3 and divides them, one obtains the relation

$$\lim_{\substack{x_1\to 0\\ x_2\to 0\\ x_3\to 1}} \alpha_{2/1} = \lim_{\substack{x_1\to 0\\ x_2\to 0\\ x_3\to 1}} \left[\frac{1+\left(\frac{V^o{}_{3V}-V^o{}_{3L}}{RT}\right)\left(\frac{\partial P}{\partial x_2}\right)_{T,x_1}}{1+\left(\frac{V^o{}_{3V}-V^o{}_{3L}}{RT}\right)\left(\frac{\partial P}{\partial x_1}\right)_{T,x_2}}\right] \qquad (18)$$

This equation is particularly helpful in the study of extractive distillation, since it indicates the maximum volatility of component 2 relative to component 1 that could be obtained by the addition of a third component 3. This value is readily obtained by measuring the terminal slopes of the binary vapor pressure vs. x curves of each of components 1 and 2 with the extracting agent. The molal volumes of the pure extracting agent in the liquid and vapor phases may usually be estimated.

EXPERIMENTAL TECHNIQUE

The apparatus used was designed to permit nearly simultaneous measurement of the vapor pressures of a pure liquid sample and of a sample of the liquid slightly diluted by the second component. Provision was made for agitation of the diluted sample. Both samples were suspended in the same constant temperature bath to minimize temperature differences between the samples. The bath temperature was controlled to ± 0.004°C. Figure 1 is a block diagram of the experimental setup.

The pure sample was contained in a Pyrex glass bulb of about 190 cc. total volume connected directly to a jacketed cistern type of mercury manometer open at the top to a high reference vacuum. The cistern was submerged in the bath, and the portion of the mercury column above the bath level was maintained at the bath temperature by circulation of the oil used as a heat transfer medium in the bath through the manometer jacket. Measurements were made after the mercury was brought in the cistern to the level of an electrical contact by means of a leveling bulb.

The diluted sample made up to a known composition in advance was contained in a Pyrex glass bulb of about 230 cc. internal volume. The sample was agitated by a magnetically driven stirrer within the bulb. The use of glass made it possible to nearly fill the bulb with a liquid sample of known composition, thus eliminating the need for analysis of the solution compositions.

The difference in the vapor pressure of the two samples was measured by means of a jacketed U-tube mercury manometer maintained at the bath temperature.

Temperatures were measured by means of a mercury-in-glass thermometer calibrated in place against the vapor pressure of pure water at temperatures in the range of interest. The vapor pressure data given in the International Critical Tables (*21*) were used for this calibration. The deviation between the temperatures derived in this fashion and the temperature indicated on the thermometer (corrected to the nearest 0.01°C. by means of a National Bureau of Standards calibration at intervals of 10°C.) had an absolute average of 0.030°C. and a standard deviation of 0.076°C. These deviations are doubtless due to the slight emergence of the mercury thread above the bath to permit reading of the thermometer. It seems fair to state that the total vapor pressures measured in this study have an accuracy corresponding to a ± 0.1°C. uncertainty in the measured temperature.

Samples of the pure materials used were placed in glass flasks with metal packless valve closures and outgased by boiling off perhaps half of the contents of the flask to a vacuum system. A satisfactorily outgassed sample would give off a metallic click as the liquid hit the valve on tipping the flask. This test is similar to that used for testing the vacuum above the mercury column in a barometer. Mixtures were made up by weight from the outgassed samples of the pure materials.

Table 1. Activity Coefficients at Infinite Dilution

2-propanol at infinite dilution in water
under the vapor pressure of water

Temperature, °C.	$\lim_{x_1\to 0}\left(\frac{\partial P}{\partial x_1}\right)_T$	$\lim_{x_1\to 0}\gamma_1$
	mm. Hg/mole fraction unit	
80.0	9,070	13.62
90.0	13,430	13.68
100.0	19,820	14.00

Water at infinite dilution in 2-propanol
under the vapor pressure of 2-propanol

Temperature, °C.	$\lim_{x_2\to 0}\left(\frac{\partial P}{\partial x_2}\right)_T$	$\lim_{x_2\to 0}\gamma_2$
	mm. Hg/mole fraction unit	
82.36	426	3.04
90.0	607	3.09
100.0	813	3.01

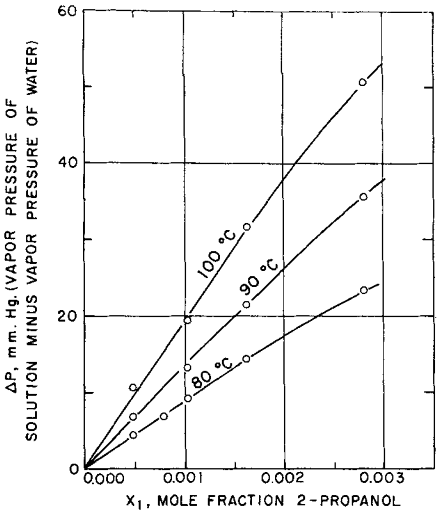

Fig. 4. Differential vapor pressure vs. liquid composition (water end).

Residual water in the 2-propanol used was determined by titrimetry. The samples were then charged as liquids to the evacuated system by means of an evacuated manifold.

The 2-propanol used was obtained as a head-cut boiling at 82.2°C. at 760 mm. Hg on distilling reagent grade material at a 10 to 1 reflux ration in a thirty plate Oldershaw column. The water used was drawn directly from the laboratory distilled-water lines.

RESULTS

The experimentally determined difference between the vapor pressure of the solution and the vapor pressure of one of the pure components are plotted in Figures 2 and 3 as their logs vs. the reciprocal of the absolute temperatures. Figure 2 is for the high water-concentration end and Figure 3 for the 2-propanol end.

Vapor-pressure difference vs liquid-composition curves in the dilute regions at several temperatures were obtained by cross plots. The results are given on Figures 4 and 5. Vapor pressure data for 2-propanol are shown in Figure 6. These data permit the calculation by Equation (12) of the activity coefficients at infinite dilution listed in Table 1.

From these values of activity coefficients at infinite dilution the Van Laar constants A and B were calculated from

$$A = \lim_{x_1 \to 0} \ln \gamma_1 \text{ at } 100^\circ\text{C.}$$

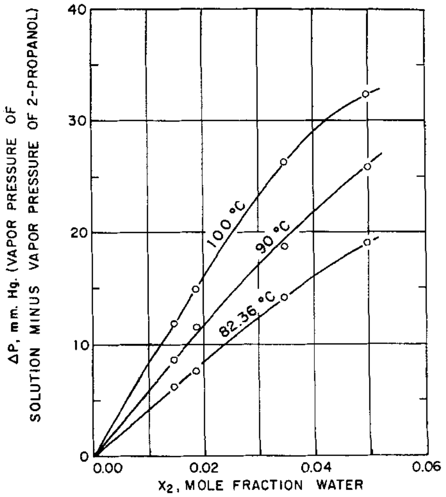

Fig. 5. Differential vapor pressure vs. liquid composition (2-propanol end).

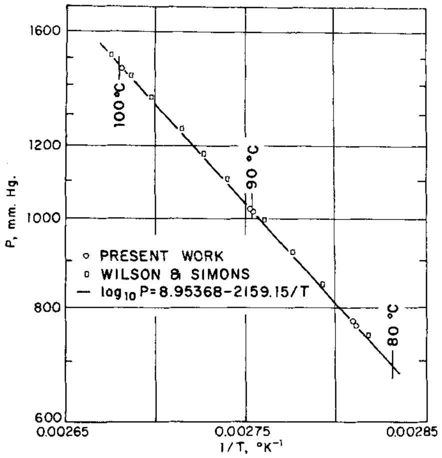

Fig. 6. Vapor pressure of 2-propanol vs. reciprocal of absolute temperature.

$$B = \lim_{x_2 \to 0} \ln \gamma_2 \text{ at } 82.36^\circ\text{C. the normal boiling point of 2-propanol}$$

Values of γ_1 and γ_2 for the full range of compositions were then calculated from Equations (8) and (9) and plotted vs. composition in Figure 7.

One also has the relations

$$y_1 P = \gamma_1 x_1 P^o{}_1 \tag{19}$$

$$y_2 P = \gamma_2 x_2 P^o{}_2 \tag{20}$$

Values of vapor composition in equilibrium with a given liquid at 1 atm. were obtained by substituting the predicted values of γ_1 and γ_2 in Equations (19) and (20) and trying various values of temperature and the corresponding values of $P^o{}_1$ and $P^o{}_2$ until $y_1 + y_2 = 1$. The results are plotted in Figures 8 and 9. It will be noted that the agreement with the experimental data of other investigators is very good. Indeed at the dilute 2-propanol end shown in Figure 9 it is likely that the predicted values are better than any single one of the other sets of data shown. This is due to the difficulty of obtaining $y - x$ data by conventional means in a highly dilute region. The use of the constants evaluated at the terminal temperatures of the isobaric y vs. x diagram insures that the predicted terminal slopes will be exact.

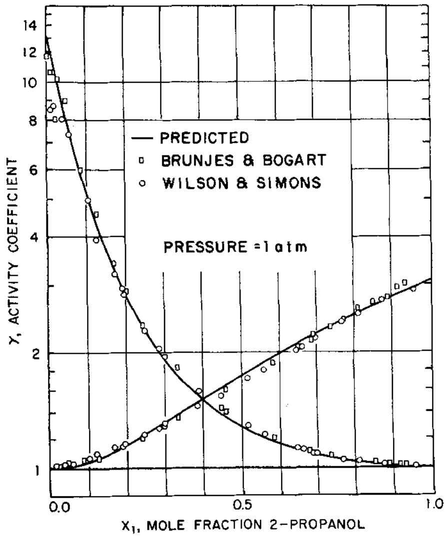

Fig. 7. Predicted activity coefficients vs. liquid composition.

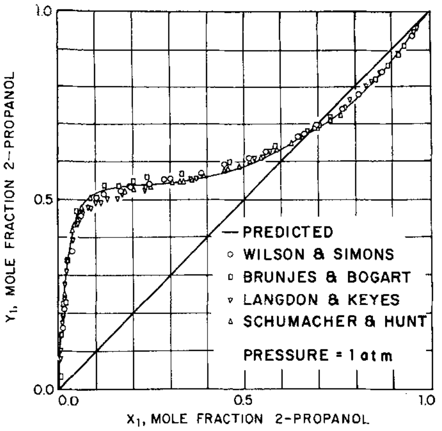

Fig. 8. Predicted vapor-liquid equilibrium values.

It should be emphasized that the fit of the data in the concentrated region predicted by the Van Laar equation is somewhat fortuitious. Other equations relating ln γ_1 and ln γ_2 to their values at infinite dilution referred to previously may be better suited to other particular system (*2*, *17*).

CONCLUSIONS

Values of the activity coefficients at infinite dilution in the 2-propanol-water system have been obtained by direct measurement of total vapor-pressure curves at several liquid compositions in the dilute regions. It is possible from these data to predict activity coefficient and vapor-liquid equilibria in the concentrated region of the Van Laar equations. Since the method yields highly accurate data in the dilute region, where more direct measurements are often difficult, the method would appear to be particularly suited to the study of extractive distillation equilibria, where normally only the extractive agent is present in high concentration in the liquid phase.

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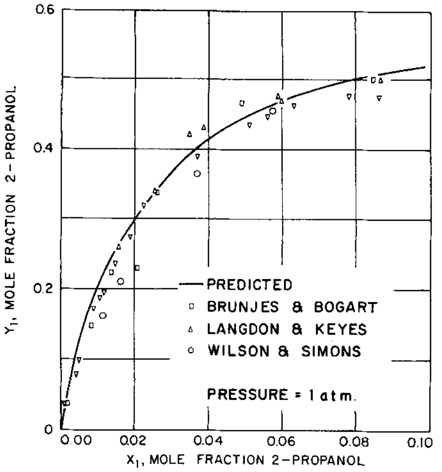

Fig. 9. Predicted vapor-liquid equilibrium values (water end).

NOTATION

A, B = empirical constants in the Van Laar equations
f = fugacity
P = pressure or vapor pressure
R = gas constant
T = absolute temperature
V = molal volume
x = liquid composition as mole fraction
y = vapor composition as mole fraction
$\alpha_{i/j}$ = volatility of component i relative to that of component j
γ = activity coefficient

Subscripts

1, 2, 3 = component designations, for the system 2-propanol-water component 1 is 2-propanol
i, j = components i, j
L = liquid phase
V = vapor phase

Superscripts

o = component in pure state

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