VAPOR-LIQUID EQUILIBRIA IN THE UNDERGRADUATE LABORATORY

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Separation and purification processes account for 70 to 90% of equipment and energy costs in modern chemical plants,[1] with distillation being among the most expensive.[2] Moreover, phase equilibrium measurements and thermodynamic modeling are key elements of chemical process design, and it is therefore not surprising that vapor-liquid equilibria (VLE) receives heavy emphasis in the undergraduate chemical engineering curriculum. Students typically learn the fundamentals of VLE and other phase equilibria as part of their thermodynamics course work, but many programs rely on a VLE laboratory exercise to reinforce and extend the knowledge gained in the classroom.

The classical undergraduate experiment involves measuring the VLE behavior of a binary mixture, often by direct compositional measurement at constant temperature and pressure. This requires charging a still with the binary system of interest and allowing the system to equilibrate, after which one records the temperature and pressure inside the still and obtains samples of both phases for compositional analysis. Common analytical techniques (*e.g.*, gas chromatography and refractive index) are time-consuming, allowing acquisition of just a few data points during a typical laboratory session and precluding a meaningful data reduction. Students therefore miss an opportunity to practice the thermodynamic modeling skills that are crucial to process design.

In a recent paper, Campbell and Bhethanabotla addressed the pitfalls of using direct compositional analysis in the undergraduate laboratory and recommended the total-pressure method as an alternative approach to acquiring VLE data.[3] This method, in which students record pressure isothermally as a function of (known) liquid composition over a wide composition range, eliminates the need for compositional analysis. Instead, vapor phase compositions are calculated by employing a suitable activity coefficient model in accordance with the method of Barker.[4] A counterpart of the total pressure method is to record isobarically the boiling temperature for multiple liquid compositions, an approach that has been in use at the University of Delaware for many years.

An important issue in any undergraduate laboratory exercise is the effective use of limited time, and time is certainly a key consideration in the industrial practice of thermodynamics where project deadlines dictate a need for the rapid acquisition of accurate VLE data.[5] Although the total-pressure method is adequate in this regard, we found that significant improvements are possible via the method of infinite dilution, isobaric ebulliometry. This method allows acquisition of data points every fifteen minutes and can be used with a modest number of data points near the compositional limits.

Given a set of four ebulliometers, groups of three students are able to measure the infinite dilution VLE behavior of two binary systems during a single laboratory session. If the two binary systems share a common component, then students can model the VLE behavior of a ternary system by combin-

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ing their experimental results with data for a third binary mixture taken from the literature. This paper describes the implementation of infinite dilution ebulliometry in the undergraduate laboratory and its application to ternary VLE.

METHODOLOGY

Ebulliometry allows measurement of VLE by the principle of liquid-phase and vapor-condensate recirculation, and Cottrell was the first to use an ebulliometer for undergraduate instruction (in 1910).[2] The Cottrell design, which used a thermal lift pump, was later modified by Swietoslawski. Although alternative designs abound, the original Swietoslawski design remains the standard in ebulliometry (for a review, see Hala[6]).

Ebulliometers operate exceptionally well with dilute solutions and allow accurate determination of infinite dilution activity coefficients, γ_i^∞. The practical definition, in our VLE context, of an infinitely dilute solution is a mixture for which the temperature changes linearly with mole fraction, and the limits of infinite dilution are specific to a given mixture. Typical limits for infinite dilution range from less than a fraction of a mole percent to several mole percent. Thus, infinite dilution ebulliometry refers to the isobaric measurement of VLE temperatures in a narrow composition range near the limit of infinite dilution rather than over a wide composition range. Working near infinite dilution limits the number of data points necessary, and the use of small aliquots avoids the need to drain and refill systems, thus conserving time.

The isobaric, infinite dilution technique involves boiling a pure liquid (solvent) of known weight and adding a very small (typically less than 0.5 mole percent), weighed amount of a second fluid (solute). The addition of solute alters the boiling point, and one records the new boiling temperature at a fixed pressure after the system reaches equilibrium. By recording the equilibrium boiling temperatures at constant pressure for several successive aliquots of solute, one obtains the dependence of boiling temperature on solute mole fraction within and slightly beyond the limit of infinite dilution. This information is sufficient to calculate activity coefficients at infinite dilution according to

$$\gamma_{\text{solute}}^\infty = \frac{P_{\text{solvent}}^{\text{vap}} - \left(\frac{dP_{\text{solvent}}^{\text{vap}}}{dT}\right)\left(\frac{\partial T}{\partial x_{\text{solute}}}\right)_{P, x_{\text{solute}} \to 0}}{P_{\text{solute}}^{\text{vap}}} \tag{1}$$

where $\gamma_{\text{solute}}^\infty$ is an activity coefficient at infinite dilution, P is the total pressure, P^{vap} is the vapor pressure, T is the absolute temperature, and x is mole fraction, where subscripts denote a given component. All qualities involving the vapor pressure are evaluated at the pure solvent boiling temperature using a readily available vapor pressure correlation (*e.g.*, Antoine, Reidel, or Harlecher-Braun)[7] The information obtained from the ebulliometric experiment is merely the limiting value of the partial derivative

$$\left(\partial T / \partial x_{\text{solute}}\right)_{P, x_{\text{solute}} \to 0}$$

and computation of the liquid phase activity coefficients at infinite dilution from Eq. (1) is straightforward.

Activity coefficients at infinite dilution become useful when one considers the criteria for VLE, namely the equality of component fugacities among phases at uniform temperature and pressure. It is customary to represent the liquid phase fugacity with an activity coefficient (as opposed to an equation of state) so that under conditions of low total pressure the equilibrium criterion for any component, i, becomes

$$x_i \gamma_i (T, P, x_i) P_i^{\text{vap}}(T) = y_i P \tag{2}$$

where x_i and y_i denote liquid- and vapor-phase mole fractions, respectively, γ_i is the liquid-phase activity coefficient, $P_i^{\text{vap}}(T)$ is the pure-component vapor pressure, and P is the total-system pressure. Pressure remains constant, the liquid-phase mole fraction is calculated by a mass balance, and vapor pressures are calculated in the manner described above. The only unknowns in Eq. (2) are the activity coefficient and the vapor-phase mole fraction. When activity coefficients are known, one can easily calculate the composition of the equilibrium vapor phase; the challenge is to evaluate the activity coefficients.

Most activity coefficient models (*e.g.*, Wilson, van Laar, two-constant Margules) for binary systems contain two system-dependent parameters, the values of which are generally unavailable. As an example, the binary van Laar model may be written

$$\ell n\, \gamma_1 = A_{12} \left(\frac{A_{21} x_2}{A_{12} x_1 + A_{21} x_2} \right)^2$$
$$\ell n\, \gamma_2 = A_{21} \left(\frac{A_{12} x_1}{A_{12} x_1 + A_{21} x_2} \right) \tag{3}$$

where subscripts 1 and 2 denote the two binary components and the parameters A_{12} and A_{21} are unknown. Under conditions of infinite dilution, Eq. (3) simplifies to

$$\ell n\, \gamma_1^\infty = A_{12}$$
$$\ell n\, \gamma_2^\infty = A_{21} \tag{4}$$

where γ_i^∞ is the activity coefficient of component i when component i is present as the (infinitely dilute) solute. Thus, the infinite-dilution technique provides a means of estimating the two model parameters, A_{12} and A_{21}, which can then be used to calculate activity coefficients and the equilibrium vapor-phase mole fraction for any liquid composition. This technique can be implemented rapidly, and the values of γ_i^∞

determined experimentally lead to fairly reasonable predictions of VLE over the entire range of binary compositions.[8] Azeotropic temperatures may be slightly over- or underestimated, but generally the composition of an azeotrope, if present, is well targeted.

Moreover, the technique allows estimates of ternary VLE when the procedure is applied to two additional binary systems with a common component. A second mixture, made of components 1 and 3, leads to the binary van Laar activity coefficient parameters A_{13} and A_{31}. Similarly, a third mixture comprising components 2 and 3 gives the binary van Laar activity coefficient parameters A_{23} and A_{32}. The six binary parameters enable calculation of activity coefficients in a ternary system comprising components 1, 2, and 3 according to the ternary van Laar model[9]

$$\ell n\gamma_1 = \frac{\left\{x_2^2 A_{12}\left(\frac{A_{21}}{A_{12}}\right)^2 + x_3^2 A_{13}\left(\frac{A_{31}}{A_{13}}\right)^2 + x_2 x_3 \frac{A_{21}A_{31}}{A_{12}A_{13}}\left(A_{12} + A_{13} - A_{23}\frac{A_{12}}{A_{21}}\right)\right\}}{\left[x_1 + x_2\left(\frac{A_{21}}{A_{12}}\right) + x_3\left(\frac{A_{31}}{A_{13}}\right)\right]^2} \tag{5}$$

A similar expression for $\ell n\gamma_2$ is obtained by interchanging subscripts 1 and 2 in Eq. (5) and for $\ell n\gamma_3$ by interchanging subscripts 1 and 3.

EXPERIMENTAL APPARATUS

Our undergraduate VLE laboratory is equipped with four ebulliometers to allow simultaneous measurement of four activity coefficients (*i.e.,* two binary mixtures). Ideally, six ebulliometers would be used for studying the ternary system, but preserving the division of labor among three students during a single laboratory session (*i.e.,* 3-4 hours) dictates a practical limit of four ebulliometers. The ebulliometers were constructed to our specifications by A.A. Pesce, Inc., and are a slight modification of the original Swietoslawski design.[6] Figure 1 shows the primary components of the ebulliometers: the boiler (A), the Cottrell pump (B), the thermowell (C), and the condenser (D).

Each ebulliometer is packed with fiberglass insulation, secured in a wooden housing, and mounted on a steel frame. The network of ebulliometers, which is set on casters for ease of transport, is positioned beneath a central fume hood for ventilation (see Figure 2). The boilers are supplied separately by four circulating hot-water baths (Fisher Scientific model 9101), and each thermowell is equipped with a platinum RTD (Omega model PR-13-2-100-1/8-12-E) and digital display (Omega model DP41-RTD). The circulating baths are controllable to within 0.1°C, and the precision of the RTDs is 0.01°C. The condensers are supplied by a central cooling system that consists of a 15-gallon polyethylene tank (Nalgene model 14100) and a centrifugal pump (Cole-Parmer model 7021). The cooling medium is an ice/water bath that is maintained at about 2°C. Ambient pressure is measured to a resolution of ±0.1 mm Hg with a centrally located mercury barometer.

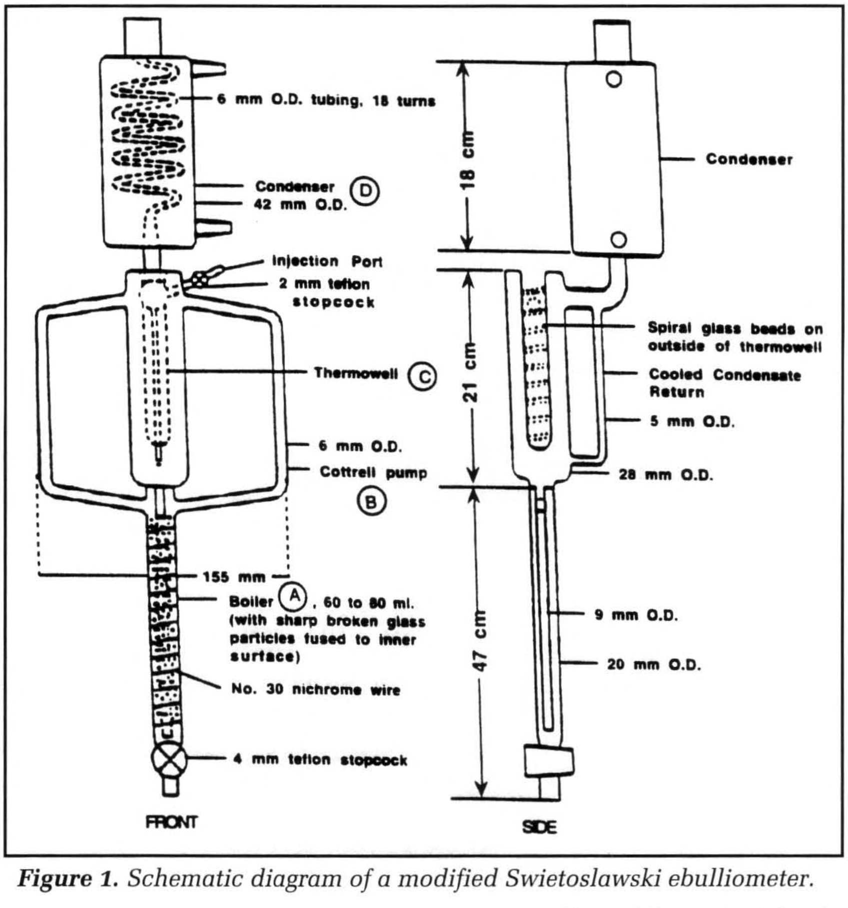

Figure 1. *Schematic diagram of a modified Swietoslawski ebulliometer.*

Operation of the ebulliometer involves charging a known mass of solvent (~60 mL) to the boiler, which can be accomplished by simply pouring the solvent from a tared beaker. The solvent is then heated to its boiling point via the circulating hot water bath. When boiling commences, rising vapors within the Cottrell arms entrain small droplets of liquid so that a two-phase flow impinges upon the thermowell. The liquid phase falls under the influence of gravity, whereas the vapors continue to rise into the condenser. Condensed vapors flow to the bottom of the thermowell, where they mix with the descending liquid phase, and all liquid returns to the boiler.

An important point to make with students is that by its very nature the ebulliometric experiment represents a steady-state process when stabilized. The intimate contacting of vapor and liquid in the Cottrell pumps, however, assures achievement of local equilibrium; boiling temperatures of pure solvents measured with the ebulliometer agree to within 0.05°C of the accepted equilibrium values.

When steady state is reached, a small aliquot (100-1000 μL) of solute is added via a gas-tight syringe through an injection port on the thermowell. This method for loading solute is necessary to avoid errors in weighing, since the solute mass must be known to within ±0.005 g to obtain values of $\left(\partial T / \partial x_{\text{solute}}\right)_{P, x_{\text{solute}} \to 0}$ with less than 1% error. This is less of a concern for the solvent mass, which requires a precision nominally one-hundred fold less than that of the solute. A new steady state is reached shortly after injecting, and the new steady-state temperature is recorded on a plot of temperature versus (liquid phase) solute mole fraction. This process is repeated until the steady-state temperature profile becomes nonlinear, indicating that the range of infinite dilution has been exceeded.

MATERIALS

Students are assigned one ternary system to be modeled on the basis of the three associated binary systems. The students are required to obtain the two activity coefficients at infinite dilution (one for each component) for each of two of the binary systems. They obtain infinite dilution activity coefficients for the third binary system from the Dechema Data Series, and we encourage students to obtain the original references cited therein.[10] Moreover, we require that students familiarize themselves with the Material Safety Data Sheets (MSDS) for each chemical that they will be using and to understand the implications of the information when performing the experiment. A wide variety of solvents can be selected, but we typically choose a combination of binary pairs that includes at least one azeotrope. Table 1 is a listing of the ternary solvent systems used in recent years at the University of Delaware. Note that several of these reagents, in particular methanol and chloroform, require careful consideration in view of safety issues associated with handling.

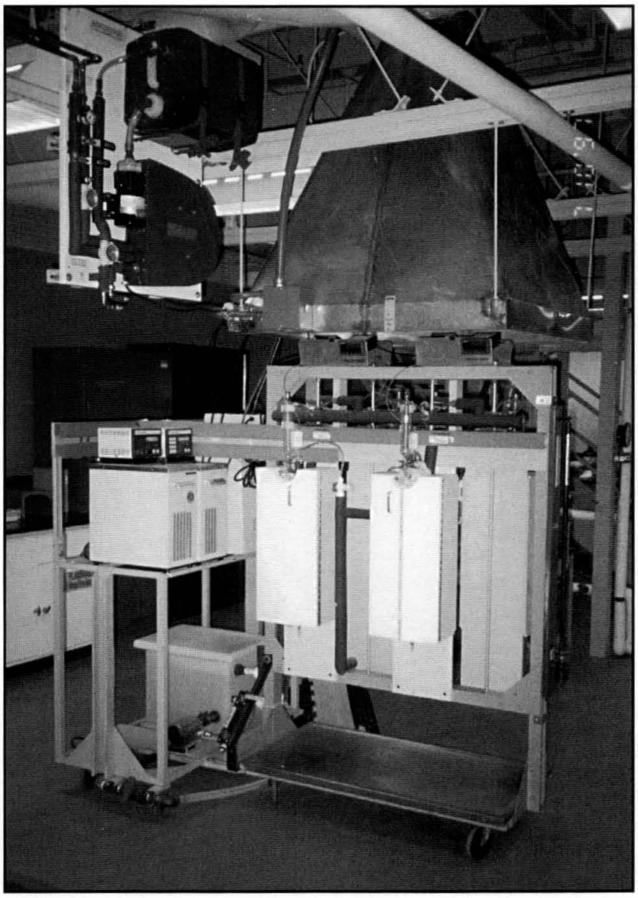

***Figure 2.** Experimental apparatus used in the undergraduate laboratory for VLE studies.*

SAMPLE EXPERIMENT

To illustrate the infinite dilution technique, we refer to an experiment from the Spring 1997 semester in which students modeled the behavior of the ternary system acetone-methyl acetate-methanol. Students made measurements on the binary systems acetone-methanol and methyl acetate-methanol, and results for the acetone-methanol binary will be shown. The raw data obtained from a single ebulliometer are provided in Figure 3. Temperature was measured continuously as a func-

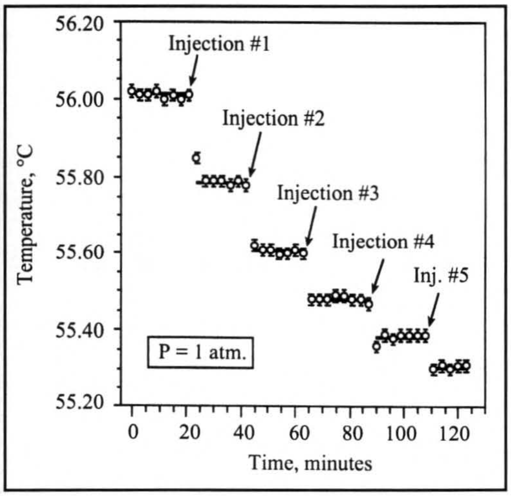

***Figure 3.** Raw data obtained from the isobaric experiment. The boiling temperature in an ebulliometer filled with acetone is recorded as a function of time as aliquots of solute methanol are added. Arrows indicate the times at which aliquots were injected, and horizontal bars denote the ensuing steady-state temperatures.*

Table 1
Solvent Systems Used in Ternary VLE Experiments

1997	Acetone	Methyl Acetate	Methanol[11]
1997	Acetone	Methanol[11]	Chloroform
1996	Isopropanol	Cyclohexane	Ethyl Acetate
1996	t-Butanol	Acetone	Hexane
1995	Ethanol	Methyl Ethyl Ketone	2-Propanol
1995	Ethanol	Acetone	Ethyl Acetate

tion of time, and values were recorded every three minutes. Arrows in the figure denote solute injections, and plateaus in the profile of temperature versus time indicate the ensuing steady states. Under these conditions the temperature at the thermowell is taken to be that of the equilibrium state as discussed earlier.

A more useful form of the results in Figure 3 is a plot of equilibrium boiling temperature versus solute mole fraction, and this is depicted in Figure 4. The plot exhibits curvature as cumulative injections begin to exceed the limit of infinite dilution. Fitting the data with a 2nd-order polynomial, the initial slope gives the desired result $\left(\partial T / \partial x_{MeOH}\right)_{P,x_{MeOH} \to 0}$, which is used to compute the infinite dilution activity coefficient, γ^{∞}_{MeOH}. The value of $\gamma^{\infty}_{MeOH} = 1.8$ was obtained using the three-constant Antoine vapor pressure correlation and leads to a value for the van Laar activity coefficient parameter of $A_{12} = 0.59$.

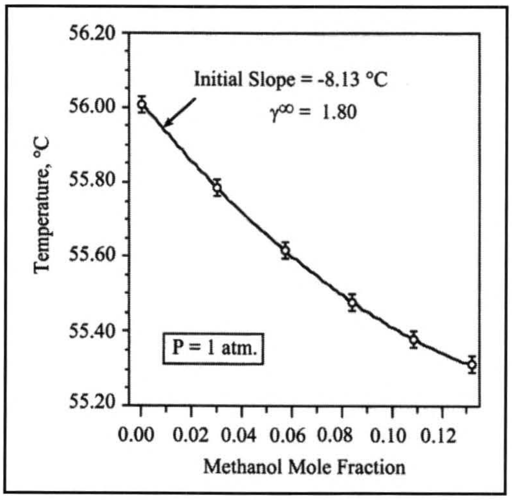

Figure 4. *Determination of infinite dilution activity coefficients. Steady-state temperatures from Figure 3 are plotted as a function of methanol liquid mole fraction. The initial slope is used to compute the infinite dilution activity coefficient for methanol via Eq. (4).*

Constructing plots similar to Figures 3 and 4, in which acetone is the solute, provides all the information necessary to estimate the full VLE behavior for the acetone-methanol binary pair. Students use that information to perform bubble-point calculations and generate a T-x-y diagram (Figure 5). The lines in Figure 5 show the acetone-methanol VLE behavior as predicted by the van Laar activity coefficient model when using the experimentally determined values of A_{12} and A_{21}. The highlight of Figure 5 is the identification of an azeotrope at a methanol mole fraction of 0.22, and students recognize the negative impact this will have on distillation. Although the partial VLE data obtained from the infinite dilution experiment are sufficient to estimate the entire VLE behavior, there is no guarantee that the predicted VLE is correct. Inaccuracies could stem from the infinite dilution measurements or from the choice of activity coefficient model that may not be suitable for the combination of solvents being studied. Students separate these effects by first comparing experimental data with accepted literature values within the range of infinite dilution. This allows a check of the ebulliometric technique itself in that it provides an estimate of the errors in the slopes $\left(\partial T / \partial x_{solute}\right)_{P,x_{solute} \to 0}$ that are used to predict the VLE at intermediate compositions.

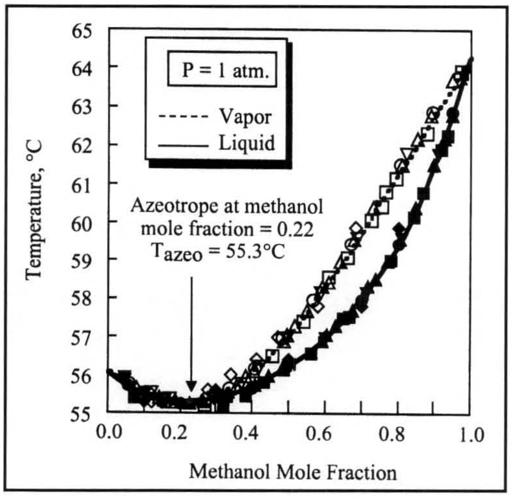

Figure 5. *T-x-y diagram showing the VLE behavior for the acetone-methanol binary system. Lines represent predictions of the van Laar activity coefficient model, based on results from the infinite dilution ebulliometric experiment. Symbols denote literature data taken from the DECHEMA series[9] (open=vapor, filled=liquid). The minimum reveals an azeotrope at a methanol mole fraction of 0.22 and a boiling temperature of 55.3°C.*

Students then test model suitability by calculating the complete VLE behavior using a variety of activity coefficient models. We require students to compare the predictive capabilities of models that assume random mixtures (*e.g.*, two-constant Margules or van Laar) with at least one model that accounts for local compositional correlations due to differences in solute-solute, solvent-solvent, and solute-solvent interactions and hence assumes non-random mixtures (*e.g.*, Wilson, NRTL, and TK-Wilson[12]). Note that the NRTL model requires a third parameter (*i.e.*, the pre-factor, A), which cannot be determined from this experiment but which tends to fall in the range 0.2<A<0.3. The symbols in Figure 5 denote the acetone-methanol VLE behavior as determined by various authors, and students are required to compare

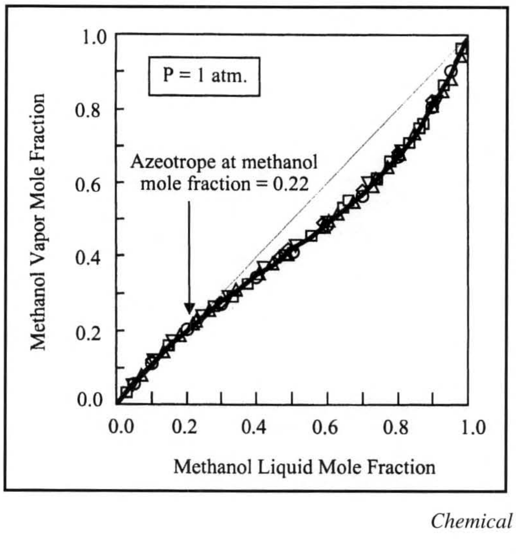

Figure 6. *x,y diagram showing the VLE behavior of the acetone-methanol binary system. Predictions from the ebulliometric experiment, using the van Laar model, are shown as a solid line. Symbols represent literature data (same as in Figure 5). The presence of an azeotrope is indicated by intersection with the 45° line.*

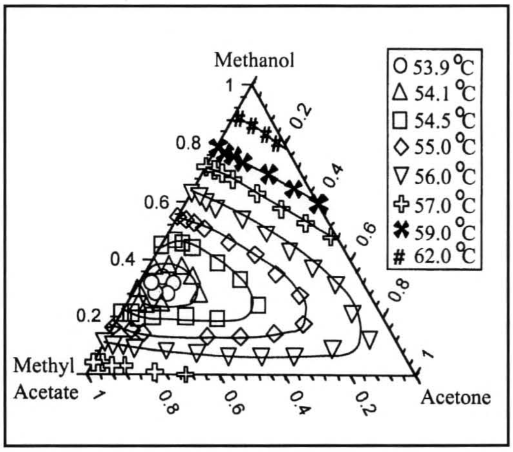

Figure 7. *Isotherms in the ternary system acetone-methyl acetate-methanol. Contours of constant temperature are plotted as a function of liquid-phase mole fractions. The isotherms converge in a "bulls-eye" fashion to reveal a ternary azeotrope at a composition of 6 mole% acetone, 62 mole% methyl acetate, and 32 mole% methanol. The azeotrope is minimum boiling at a temperature of 53.9°C.*

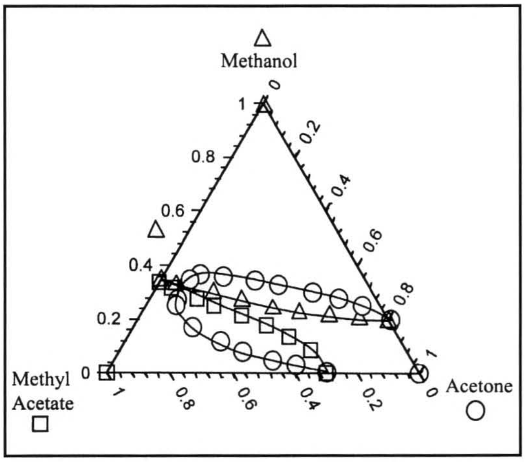

Figure 8. *Contours of K_i=1 in the ternary system acetone-methyl acetate-methanol. Contours of the partition coefficient, K_i, are plotted for each component in the case where each partition coefficient is one. Thus, the mole fraction of any component is the same in both phases along the contour for that component. The intersection of two contours, along the edge in which the mole fraction of the third component is zero, represents a binary azeotropic composition. The intersection of all three contours indicates the presence of a ternary azeotrope at a composition of 7 mole% acetone, 61 mole% methyl acetate, and 32 mole% methanol.*

the predictions of each activity coefficient model with the literature studies. Any variation in the goodness-of-fit between models, as compared with both the infinite dilution data obtained by the students and the literature data at intermediate compositions, requires students to consider which model best captures the physical differences (*e.g.,* size or polarity) between solvent and solute molecules.

Another way in which students check their results with literature studies is in the form of an x,y diagram (see Figure 6), identical to those used to construct McCabe-Thiele diagrams when sizing distillation columns. Lines again represent model predictions, and symbols denote literature studies. It is pleasing that the azeotrope obtained in Figure 6 matches that of Figure 5 as it should, but it is not uncommon (although it is not the case here) for predicted azeotropes to agree more favorably with literature compositions than with temperatures. Over the years we have found that the ebulliometric method leads to azeotropes that are nearly always correct in composition, but not necessarily correct in temperature, and this is true regardless of which activity coefficient model is used.

We attribute the above phenomenon to the presence of systematic errors that affect measurements in all four ebulliometers to nearly the same extent. This implies that variations in performance among the individual ebulliometers are not the dominant source of systematic errors. Thus, the slopes that are measured at infinite dilution for a given binary system are either both greater than or both less than the accepted values, and the magnitudes of the deviations are similar. Seldom is the case in which the error of one slope is positive and the other negative, which would of course skew the predicted azeotrope composition. This is yet another way in which students distinguish between errors in the measurements and model suitability.

Having analyzed the experimental errors and model validity in this way, students must then decide if the predicted VLE behavior is acceptable or if a complete VLE study is warranted. Thus, students learn to weigh the need for accuracy against limited resources, a lesson that will serve them well in industry.

TERNARY SYSTEM

The culmination of experimental and modeling efforts is the generation of ternary-phase diagrams. Using the four binary activity coefficient parameters they determined experimentally, in addition to two taken from the literature, students perform ternary bubble-point calculations with an activity coefficient model of their choice to create plots like those in Figures 7 and 8. Both are triangular diagrams, in which each apex denotes a pure component, and any point within the triangle represents a particular liquid-phase composition.

The series of points in Figure 7 correspond to various isotherms, and the "bulls-eye" pattern indicates the presence of a ternary azeotrope. In this case the azeotrope occurs at a composition of 6% acetone, 62% methyl acetate, and 32% methanol (all mole %) and boils at 53.9°C. This azeotrope is therefore minimum boiling, although it is possible to obtain maximum boiling and saddle-point azeotropes with other ternary systems, or no azeotrope at all.

Identification of azeotropes is a key factor when considering distillation, and students address the feasibility of separation by plotting contours of constant K_i for each component, where K_i (the distribution coefficient) is

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defined by $K_i=y_i/x_i$. Of special interest is a plot of contours for $K_i=1$, as shown in Figure 8. Since points at which $K_i=1$ indicate that the mole fraction of a particular component is identical in both phases, any point at which the three individual $K_i=1$ contours intersect defines a ternary azeotrope. Thus, Figure 8 contains a ternary azeotrope at a composition of 7% acetone, 62% methyl acetate, and 31% methanol, in good agreement with Figure 7 and indicating self-consistency in the students' calculations. Certainly, the ternary plot should also predict any binary azeotropes. For example, the intersection of $K_i=1$ contours for acetone and methanol, along the edge in which the methyl acetate mole fraction is zero, reveals an acetone-methanol binary azeotrope at a methanol mole fraction of 0.2. This result is in excellent agreement with that of Figures 5 and 6.

OTHER CONSIDERATIONS

A technical detail to consider when planning the experiment outlined in this paper is the requirement for constant pressure. Whereas the data reduction (specifically, Eq. 4) assumes constant pressure, the actual system pressure is subject to atmospheric changes. Occasionally, students may face the challenge of performing the experiment as a storm front approaches and the atmospheric pressure changes appreciably. It is therefore imperative that students be able to handle pressure fluctuations, either during data reduction by modification of Eq. (4) to include a pressure dependence or (preferably) by correcting the measured boiling points for changes in pressure during the lab session. Even if the correction turns out to be negligible, good engineering practice requires that this be tested rather than assumed. We therefore view systematic pressure variation as a fortunate event because it affords students the opportunity to think through the aberration and account for the effect.

Finally, a remaining consideration that may be of critical concern is one of cost. Price quotes for the main components in our system are $800 (Swietoslawski ebulliometer), $1900 (hot water circulator), $650 (digital temperature display), $120 (pump), $125 (HDPE tank), and $130 (platinum RTD).[13] The capital cost for a simple VLE experiment involving a single ebulliometer is therefore approximately $3700 (plus associated piping), although time limitations would likely limit such an experiment to a single binary system. Reproducing the ternary VLE experiment we have described requires a capital expenditure on the order of $15,000.

CONCLUSIONS

Our undergraduate VLE experiment has evolved over several decades and has been in its current form the past five years. We believe that it is unique because it allows generation of ternary phase behavior from a single afternoon of data collection.[14] The lab is therefore educational in two very important general aspects. One is the technical training that the lab provides, since students demonstrate a greatly improved understanding of phase behavior and sharpen their modeling skills as a direct result of the laboratory work. Another is the practical lesson students learn; that time and money are important considerations when planning any experiment, and reasonably accurate data can often be obtained without elaborate measurement techniques.

We invite you to visit our VLE website at
http://www.che.udel.edu/cheg345

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14. The lab operates on a four-week cycle. During week 1 students view the equipment and complete a pre-laboratory homework assignment. The experiment is performed by five teams (each with three students) during week 2, where each team is given one afternoon session (typically 3-4 hours) to obtain data. Students prepare a preliminary technical report during the third week that addresses only the binary VLE data and modeling. The ternary system is handled during week 4, in which students prepare a final technical report that addresses the feasibility of separating the three chemicals. ❐