Vaporization Ratio in Differential Ebulliometers for Measuring Limiting Activity Coefficients

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Accurate limiting activity coefficients can be obtained from differential ebulliometry if vapor and liquid holdups in various parts of the equipment are correctly accounted for in calculating the equilibrium liquid composition from the known charge composition. Available procedures require the difficult-to-determine dynamic vaporization rates (V/F) *or* (V/L)*. Two new procedures proposed determine* V/F $(=\phi)$*: 1. a trial-and-error procedure satisfying all three of the equations governing the ebulliometer operation yielding the true liquid equilibrium composition* x_1, ϕ*, and the overall composition in the Cottrell pump,* Z_1*; 2. one procedure based on the measured superheat temperature at the base of the Cottrell pump. A possibly limiting assumption is that local equilibrium exists at this point, but the method has good rigour otherwise. It is, however, very sensitive to measured pressures and temperatures, which need to be of the highest accuracy. The procedure is illustrated for the n-hexane (1)−ethanol (2) and n-hexane (1)−ethylacetate (2) systems, and requires liquid density, heat capacity and accurate latent heats over a small temperature interval. Measurements suggest that about 72% of the total vaporization takes place at or before the entrance to the Cottrell pump with only about 28% in the equilibrium chamber for the n-hexane−ethyl acetate system. For the n-hexane−ethyl alcohol systems, they are 89% and 11%. The iterative procedure is recommended because it is more reliable and, although computationally extensive, has more rigor.*

Introduction

In distillation equipment design for high-purity products, accurate phase-equilibrium data in the very dilute regions are both crucial and generally the most difficult to measure. Limiting-activity coefficients, γ_i^∞, provide the best representation in these regions and several methods have been developed for their accurate measurement. Differential ebulliometry provides an attractive route, but it has been largely limited to systems of small to moderate relative volatility due to the difficulty in finding the true liquid equilibrium concentration, x_1, from the charge composition, x_{s1}. A system of three exact equations, governing concentrations and liquid and vapor holdups in a dynamic ebulliometer (Raal, 2000) permits determination of x_1 from the accurately known x_{s1} through a dimensionless ebulliometer "constant" E

$$x_1 = \frac{x_{s1}}{1+(K_1-1)E} \tag{1}$$

where

$$E = V'/S' + (R'/S')\phi \quad \text{and}$$

$$K_1 = \text{Equilibrium constant} = y_1/x_1, \tag{1a}$$

E is seen to depend on the normalized "static" vapor and reboiler holdup quantities (V'/S') and (R'/S'), and, importantly, on the dynamic vaporization ratio ϕ $(=V/F)$. The "static" holdups reflect the distribution of the charge, S' moles, in the equipment at any instant after equilibrium has been reached and can be determined from Eq. 1a by plotting E vs. ϕ. Characterization of an ebulliometer in this way requires measurement of the composition of the combined liquid−vapor condensate stream Z_1 using a sampling point such as is shown in Figure 1. The iterative calculation procedure

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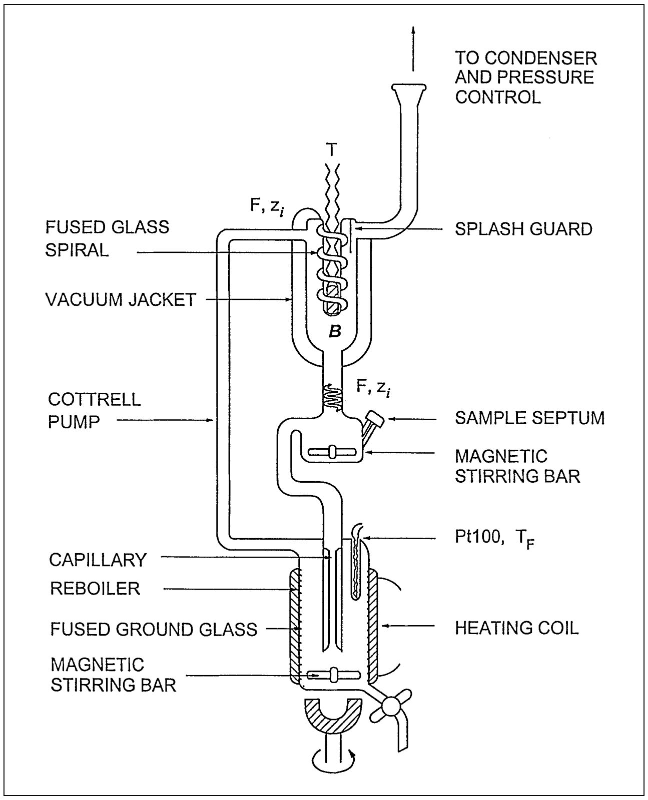

Figure 1. Ebulliometer with sampling point in liquid downcomer.

has been given in detail (Raal, 2000). The vaporization ratio, ϕ, is, however, a remarkably elusive quantity and the equation proposed for its estimation from the measured superheat temperature, T_s (Eq. 14b in Raal) is not satisfactory. In their analysis of ebulliometer operation, Dohnal and Novotna (1985) obtained estimates of $f = \phi/(1-\phi)$ averaged at 0.06 from analysis of several systems, by neglecting liquid holdup. The same value (0.06) also with fixed values for $V'/S' = 0.02$ and $L'/S' = 0$ was subsequently used for determining γ_1^∞ from $\Delta T - x_{s1}$ measurements for other systems. Rogalski et al. (1977) used three different procedures for finding f. These included measuring drop rates of liquid and condensed vapor in a modified ebulliometer separately, sampling liquid and vapor phases, and a fitting procedure for a system of known phase-equilibrium behavior. Only the latter was considered satisfactory. Calculations were based on a flash equation in which Z_1 is equated with the charge composition, x_{s1}. It is not clear what f value should be used for a new system of different physical characteristics. The compositions Z_1 and x_1 can differ considerably, as shown below for our measurement on the n-hexane–ethyl acetate system.

The principal purpose of this article is to explore more rigorous procedures for finding f or ϕ, and two such methods are given below.

Determination of ϕ from "Superheat" Measurements

Application of the macroscopic energy balance from point 1, at the base of the Cottrell pump, to point 2, where it discharges onto the thermometer well gives (neglecting kinetic energy effects and heat loss to the environment),

$$g\Delta Z + H_2 - H_1 = 0. \tag{2}$$

In terms of the molar flows F, V, and L, and mass flow rate, $\dot{m}$ (with $F = V + L$), Eq. 2 becomes

$$VH_v + Lh_L - Fh_F = -g(Z_2 - Z_1)\dot{m}.$$

In terms of ϕ ($= V/F$), this becomes

$$[\phi H_v + (1-\phi)h_L]_{T,p} - [h_F]_{T_s,p_s} = g(Z_2 - Z_1)M \tag{3}$$

The molar flow at the entrance to the Cottrell pump contains a fraction m_2/F of vapor, and this must be accounted for in the term $[h_F]_{T_s,p_s}$,

$$(h_F)_{T_s,p_s} = [(m_2/F)H_v + (1 - m_2/F)h_L]_{T_s,p_s}.$$

Substitution into Eq. 3 gives

$$\phi(H_v - h_L)_{T,p} + (h_L)_{T,p} - (h_L)_{T_s,p_s} - (m_2/F)[H_v - h_L]_{T_s,p_s} = -g\Delta ZM.$$

In terms of latent heats, λ_T and λ_s, at temperatures T and T_s, and neglecting the influence of pressure on liquid enthalpy,

$$\phi\lambda_T - \bar{C}_{P_L}(T_s - T) - (m_2/F)\lambda_s = -g\Delta ZM.$$

thus,

$$\phi = \frac{\bar{C}p_L(Ts - T) + (m_2/F)\lambda_s - g\Delta ZM}{\lambda_T}. \tag{4}$$

The latent heats in Eq. 4 are mixture latent heats, but for very dilute solutions may be taken as those for the pure fluid.

All terms in Eq. 4 are known or can be estimated, except the fractional vapor rate (m_2/F) at the entrance to the Cottrell pump, and it appears that one problem (determination of ϕ (has been replaced by another similar one, finding (m_2/F). No obvious relationship between (m_2/F) and ϕ is evident. Their ratio represents the vapor fraction at the entrance to the Cottrell tube to that in the equilibrium chamber when superheat has been discharged. If a correlation between ϕ and (m_2/F) was available, Eq. 4 would present a powerful noniterative and independent procedure for finding ϕ for use in Eq. (1). However, ϕ can be related to (m_2/F) by the following consideration (see Figure 2).

Where the Cottrell pump discharges, vapor and liquid are assumed to be in dynamic equilibrium so that

$$\phi = \left[\frac{Z_1 - x_1}{y_1 - x_1}\right]_{T,p}, \qquad Z_1 = \text{overall mole fraction}. \tag{5}$$

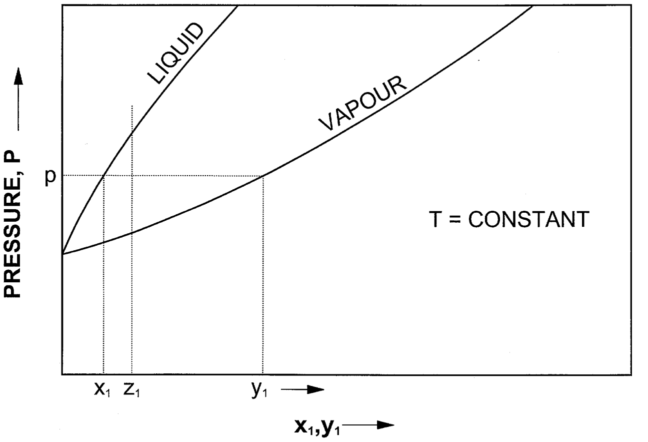

Figure 2. Equilibrium concentrations.

If it is also assumed that vapor and liquid are in equilibrium at the entrance to the Cottrell tube (a less satisfactory assumption, but not unreasonable if the reboiler is well-stirred mechanically), a diagram similar to that of Figure 2, but slightly displaced at temperature, T_s, will apply, with

$$\left(\frac{m_2}{F}\right)=\left[\frac{Z_1-x_1'}{y_1'-x_1'}\right]_{T_s,p_s} \tag{6}$$

Elimination of the overall composition Z_1 (which remains constant in the Cottrell tube) from Eqs. 5 and 6, and in terms of the equilibrium constant K, gives

$$\begin{aligned}\left(\frac{m_2}{F}\right)&=\phi\left[\frac{K_1-1}{K_1'-1}\right]\frac{x_1}{x_1'}+\frac{(x_1/x_1')-1}{(K_1'-1)}\\&=\phi B+A \quad \text{(for convenience).}\end{aligned} \tag{7}$$

Equation 4 finally becomes

$$\phi=\frac{\bar{C}p_L(T_s-T)-g\Delta ZM+\lambda_s A}{\lambda_T-B\lambda_s} \tag{8}$$

Evaluation of the concentration ratios A, B

To be useful in practical ebulliometry, satisfactory estimates of the concentration ratios

$$A\left[=\left(\frac{x_1/x_1'-1}{K_1'-1}\right)\right] \quad \text{and} \quad B\left[=\left(\frac{K_1-1}{K_1'-1}\right)\frac{x_1}{x_1'}\right]$$

must be obtained. At the entrance to the Cottrell pump (where the liquid is superheated with respect to the equilibrium temperature, T, at the thermometer well) local equilibrium has been assumed and the pressure of the well-stirred liquid can be given in terms of activity coefficients and the local liquid composition, x_1'

$$p_s=\Sigma y_i'p=\Sigma\frac{x_i'p_i^{\text{sat}}\gamma_i}{\Phi_i}.$$

Solving for x_1', and with the correction factors $\Phi_i=1$ (permissible at low pressures) gives

$$x_1'=\left[\frac{p-\gamma_2p_2^{\text{sat}}}{\gamma_1p_1^{\text{sat}}-\gamma_2p_2^{\text{sat}}}\right]_{T_s,p_s} \tag{9}$$

Since T_s is measured (see Figure 1), the saturation pressures, p_1^{sat} and p_2^{sat}, will be known. In the very dilute region, $\gamma_2(x_1)\approx 1.0$, and only p_s and $\gamma_1(x_1')$ must be evaluated. The superheat pressure, p_s, can be determined from the measured temperature T_s. With pure solvent in the ebulliometer

$$p_s^{\text{sat}}=p+\rho g\Delta Z_{\text{eff}} \tag{10}$$

ΔZ_{eff} is used here since it can also contain a correction for effective density. In Eq. 8 ΔZ is generally negligible in comparison with the other two terms. Determination of p_s^{sat} at T_s from an Antoine-type equation for the solvent gives ΔZ_{eff}, which, once determined, can then be used with Eq. 10 to find p_s for dilute solutions. The addition of a very small amount of solute to the ebulliometer should not affect the value of ΔZ_{eff}, but may be accounted for as well as any volume reduction by sampling. If several ebulliometers connected to a common manifold are used, they should be filled to the same level as the one containing pure solvent. Frictional loss in the Cottrell tube has been neglected in Eq. 10, since its inclusion for a two-phase mixture seems an unjustifiable elaboration. Its effect is, however, taken into account insofar as its influence is reflected in p_s, that is, contained in the measured temperature, T_s. The pressure in the ebulliometer at the level where T_s is measured can, of course, also be measured with a pressure transducer connected at this point, but this increases the equipment cost considerably. Finally, $\gamma_1(x_1')$ must be determined. In the iterative procedure for finding γ_1^∞ for a new system (Raal, 2000), improved estimates of the liquid equilibrium composition, x_1, are generated successively, starting with the known charge composition, x_{s1}. The activity coefficient at T, p is then generated conveniently from a one-constant equation, in the simplest case, the Margules two-suffix equation: ln $\gamma_1=Ax_2^2$, with $A=\ln\gamma_1^\infty$.

To calculate γ_1 (x_1') at T_s and p_s, the effect of the generally small difference in temperature (between T_s and T) can usually be neglected, and the influence of pressure will be negligible. The liquid concentration x_1' at T_s, p_s can thus be determined from Eq. 9 using γ_1 (x_1), and hence also K_1'(= $[(\gamma_1p_1^{\text{sat}}/p]_{T_s}$). Equation 9 lends itself to a simple, rapidly convergent iterative procedure to determine improved x_1'(values using a trial value (e.g., x_1) to determine $\gamma_1(x_1)$ in the denominator.

If the temperature, T_s, is appreciably higher than T, its effect on γ_1 can be taken into account by using the one-constant Wilson equation, which has a limited intrinsic temperature dependence. This equation has been shown to give a remarkably accurate representation of activity coefficients in the dilute regions for highly nonideal systems (Raal and Ramjugernath, 2001).

The preceding procedure for finding ϕ requires accurate values for the latent heats at the equilibrium and "superheat" temperatures (T, T_s), liquid heat capacity Cp_L, and liquid density at the operating temperature. It is not unduly complex, but is very sensitive to the measured pressures, temperatures, and to the value of ΔZ_{eff} in Eq. 10. Small errors in p_i^{sat}, p, T, or T_s can easily produce physically unrealistic values for ϕ or m_2/F (the fractional vapor rate at the entrance to the Cottrell pump). A disadvantage of the procedure is evident in that a good estimate of the equilibrium liquid composition, x_1, is required, but this is exactly the quantity to be determined from Eq. 1 to find an improved γ_1^∞ ultimately!

The procedure is illustrated below for the highly nonideal *n*-hexane (1)–ethanol (2) system, and in more detail for the *n*-hexane (1)–ethyl acetate (2) system.

Example 1: Calculation of ϕ and m_2/F, n-hexane – ethanol system

Experimental measurements, made on the apparatus of Figure 1 for the system *n*-hexane (1)–ethanol (2) with ethanol as the solvent, at a pressure of 9.6 kPa, will be used to illustrate the calculational procedure. This system is a difficult choice, first because the relative volatility is high so that the correction for x_1 is large, but also because the temperature–pressure sensitivity, as represented by $(\delta T/\delta p)_x^\infty$, is substantial. The latter quantity is given for the very dilute region (Joseph et al., 2002) by (This reduces to $(dp_2^{sat}/dt)^{-1}$. An expression for $(\partial T/\partial P)$ at finite concentrations has, however, been developed by Raal and Ramjugernath (2003) and shows a small, monotonic increase with concentration)

$$(\partial T/\partial p)_x^\infty = \frac{-(\partial T/\partial x)^\infty}{\gamma_1^\infty p_1^{sat} - p_2^{sat}} = 0.195\text{K/mbar} \qquad (11)$$

Pressure control of ~ 0.05 kPa (0.5 mbar) by a commercial pressure controller, such as used in the study, can therefore produce temperature fluctuations unrelated to composition change of nearly 0.1 K. Temperature and pressure measurements were made with Pt-100s and with a Sensotec TJE pressure transducer, with calibrations traceable to NIST standards.

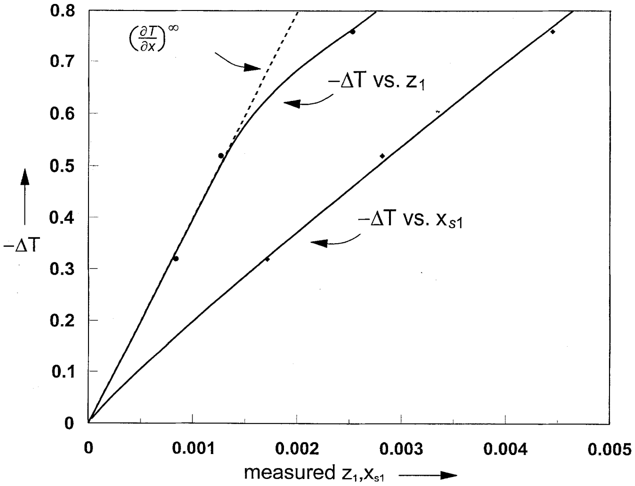

Figure 3. Measured temperature differentials for *n*-hexane(1)–ethanol(2) system at 301.7 K.

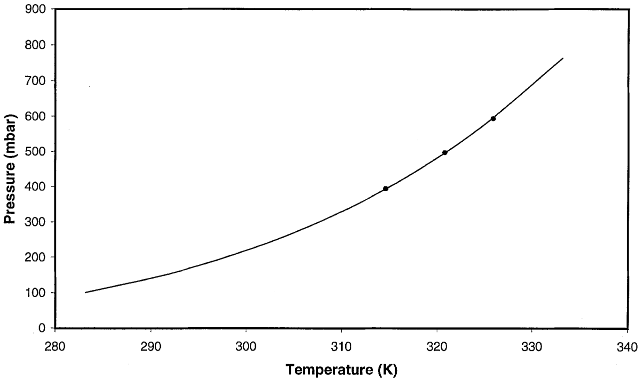

Figure 4. Measured vapor pressure data for *n*-hexane.

Literature data:—Reid et al. (1988).

Using the calculation procedure of Raal (2000), with measurement of the composition, Z_1, gave the following ebulliometer characterization (cf. Eq. 1)

$$E = 0.969\,\phi + 0.026. \qquad (12)$$

(This characterization, based on an average value of $\gamma_1^\infty = 11.2$ in the literature, is itself a difficult proposition, very sensitive to small errors in measured pressure or composition.) Measured $\Delta T - x_{s1}$ and $\Delta T - Z_1$, data are shown in Figure 3. Property data required for the calculation of ϕ are as follows:

$Cp_{L2} = 113.8$ J/mol (Reklaitis, 1983)
$\rho_2 = 0.780$ g/cm^3 (Reid et al., 1988)
$\lambda_s = 43{,}215$, $\lambda_T = 43{,}570$ J/mol [from Perry and Green, 1985 and the Watson equation as given in Reid et al. (1988) for the effect of temperature].

Pure component vapor pressures were calculated from Antoine equation data (Reid et al., 1988), which were in good agreement with measured data (see, for example, Figure 4 and Table 1).

Determination of pressure p_s and ΔZ_{eff}

With pure ethanol in the apparatus, the measured temperatures T and T_s were 28.471°C and 30.275°C (301.621 K and 303.425 K, respectively) and the pressure $p = 9.611$ kPa (Bedassi, 2001). The saturation pressure p_2^{sat} corresponding to T_s is $p = 10.631$ kPa. From Eq. 10,

$$10.631 = 9.611 + \rho g \Delta Z_{eff},$$

giving $\Delta Z_{eff} = 0.1334$ m = 13.34 cm. (The actual length of the Cottrell tube was 26.0 cm.)

Table 1. Measured Vapor-Pressure Datas vs. Literature Values

Press. (kPa)	Temp. (K)	T^* (K)	$T_{exp} - T_{Lit}$
49.62	320.80	320.80	0.00
59.30	325.88	325.78	0.10
39.34	314.63	314.58	0.05

*From Reid et al. (1988).

Calculation of x_1' and concentration ratios A, B

The limiting slope of the plot of $-\Delta T$ vs. Z_1 in Figure 3 (~ 435 K) produces a value for $\gamma_1^\infty = 10.56$. This is close to an average value of about 11.2 from literature sources (which show considerable scatter) and suggests that the equilibrium liquid composition, for example, for the intermediate data point will be about 0.001, that is, slightly less than Z_1.

For purposes of illustration we will assume $x_1 = 0.001$ and calculate ϕ for this point. (This liquid composition corresponds to a total pressure $p = \Sigma x_i \gamma_i p_i^{\text{sat}} = 9.594$ kPa, in close agreement with the measured pressure, $p = 9.607$ kPa). Calculation of x_1, A, B, and ϕ from Eqs. 8 and 9 with $\Delta Z_{\text{eff}} = 0.1334$ gave a *negative* value for ϕ.

The calculation is very sensitive to the value of ΔZ_{eff}, which must be determined with considerable accuracy. A reduction of only 0.50 cm, for example, due to a slightly different operating liquid level in the Cottrell tube due to net sample removal of 0.15 cm^3 or to an error in the measured pressure of only 0.04 kPa, produces realistic results. The calculation is given in detail below for $Z_{\text{eff}} = 0.1284$. From Eq. 9

$$x_1' = \left[\frac{p - \gamma_2 p_2^{\text{sat}}}{\gamma_1 p_1^{\text{sat}} - \gamma_2 p_2^{\text{sat}}}\right]_{T_s, p_s}.$$

For the second data point (Bedassi, 2001),
$T = 27.989°\text{C} = 301.139$ K; $p_1^{\text{sat}} = 22.926$ kPa
$p = 9.607$ kPa
$T_s = 29.746°\text{C} = 302.896$ K

At T_s, $p_1^{\text{sat}} = 24.6848$ kPa, $p_2^{\text{sat}} = 10.323$ kPa. For an estimated $\gamma_1^\infty = 10.56$ (from Figure 2), ln $\gamma_1^\infty = A = 2.3571$ in the Margules equation, that is,

$$\ln \gamma_1 = A x_2^2 = 2.3571\ (0.999)^2 \tag{13}$$

$$= 2.3524,$$

$$\gamma_1(x_1) = 10.5106$$

and

$$K_1 \approx \frac{\gamma_1 p_1^{\text{sat}}}{p} = \frac{(10.5106)(22.926)}{9.6074} = 25.0823.$$

thus

$$p_s = p + \rho g \Delta Z_{\text{eff}}$$

$$= 9.607 + 0.780\ (9.8)(0.1284)$$

$$= 10.589 \text{ kPa}.$$

At this pressure

$$K_1' = \left[\frac{\gamma_1 p_1^{\text{sat}}}{p}\right] = \frac{(10.5106)(24.6848)}{10.589}$$

$$= 24.5020.$$

Thus, from Eq. 9,

$$x_1' = \frac{10.589 - (1.0)(10.323)}{(10.5106)(24.6848) - 10.323}$$

$$= 0.00107.$$

This value remained unchanged after one iteration (that is, using the new value of x_1' to recalculate $\gamma_1(x_1')$ and x_1' from Eq. 9.

The concentration ratios A and B become

$$A = \frac{(x_1/x_1') - 1}{K_1' - 1} = -0.00257$$

$$(K_1' = 24.5020)$$

$$B = \left(\frac{K_1 - 1}{K_1' - 1}\right)\left(\frac{x_1}{x_1'}\right) = \left(\frac{24.0823}{23.5020}\right)\left(\frac{0.001}{0.00107}\right)$$

$$= 0.9577.$$

Finally, calculate ϕ from Eq. 8

$$\phi = \frac{(113.8)(1.757) - (9.8)(0.1284)(46)\times 10^{-3} - (0.00257)(43215)}{43{,}570 - (0.9577)(43215)}$$

$$= \frac{199.95 - 0.06 - 111.063}{43{,}570 - 41{,}387}$$

$$= 0.0409.$$

This value is physically reasonable and only slightly lower than that obtained in the ebulliometer characterization procedure (0.043), based on the average literature value for γ_1^∞ of 11.2. The latter value for ϕ is itself subject to some uncertainty. The fractional vapor rate at the entrance to the Cottrell tube, (m_2/F), can also now be calculated

$$(\text{m}_2/F) = A + B\phi = -0.0026 + 0.9577\ (0.0409)$$

$$= 0.0366.$$

Example 2: n-hexane (1)–ethyl acetate (2) system

Smooth values of γ_1^∞ vs. temperature are available for the system from Thomas et al. (1982). The temperature–pressure sensitivity of the system $(\partial T/(\partial p)^\infty$, 0.074 K/mbar, is lower than for the hexane–ethanol system, but pure ethyl acetate produced somewhat bumpy boiling. Measured $(-\Delta T)$ vs. x_{s1} are shown in Figure 5 and in Table 2, from which a first approximation of $\gamma_1^\infty = 2.294$ was obtained [cf. Thomas et al. (1982) value of 2.85 by interpolation]. In exploring this system, it was found that solutions satisfying all three independent equations governing ebulliometers (Raal, 2000) could be obtained by iterative procedures. These yielded the values of x_1, ϕ, and Z_1 for the three experimental points shown in Table 2. The $(-\Delta T) - x_1$ sets gave an exact fit to the quadratic

$$-\Delta T = 70.0194 x_1 + 2401.98 x_2 \tag{14}$$

from which $(\partial T/(\partial x_1)^\infty = 70.0194$ and $\gamma_1^\infty = 2.838$. This value is in excellent agreement with the Thomas et al. (1982) value just given. The equipment characterization equation, with constants obtained for the hexane–ethanol system, was used

$$E = (R'/S')\phi + (V'/S') = 0.969\phi + 0.026 \tag{15}$$

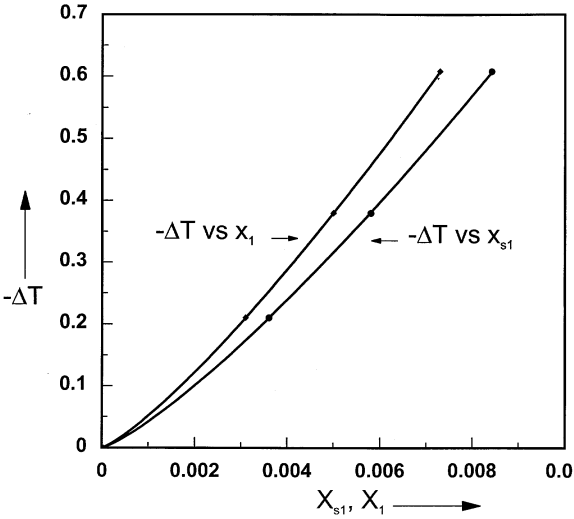

Figure 5. Measured temperature differential vs. charge composition (x_{s1}) and true liquid equilibrium composition (x_1)

[Inspection shows that the dimensionless ebulliometer holdups (R'/S') and (V'/S') should remain essentially constant for all systems if the ebulliometer has the same volume of liquid at operating conditions (~ same volume of charge).] In addition to holdups (R'/S') and ($V'/S')'$ values, the procedure requires only the pure-component vapor pressures and constitutes a powerful new method, since the results satisfy the three rigorous and exacting equations governing ebulliometry.

New iterative procedure for ϕ, x_1, and Z_1

The iterative scheme developed is briefly as follows:

(1) Estimate a trial value of γ_1^∞, for example, somewhat larger than the value obtained from $(\partial T/(\partial x_{1s})^\infty$, depending on the relative volatility of the system.

(2) Calculate the constant in a one-parameter equation for γ_1, for example, $\ln \gamma_1(x_1) = Ax_2^2$, $A = \ln \gamma_1^\infty$.

(3) Estimate a value for x_1, for example, somewhat smaller than x_{s1}.

(4) Calculate the system pressure, $P_\Sigma = \Sigma x_i \gamma_i p_i^{\text{sat}}$, and compare with the measured pressure P_{exp}. (If P_{exp} cannot be obtained with a realistic value of x_1, choose a larger or smaller value for γ_1^∞).

(5) Assume a value for ϕ and calculate E from Eq. 12.

(6) Calculate $K_1(=\gamma_1 p_1^{\text{sat}}/P)$ and then Z_1 from

$$z_1 = x_{s1}\left\{\frac{1+(K_1-1)\phi}{1+(K_1-1)E}\right\} \tag{16}$$

(7) Recalculate ϕ from

$$-\phi = \frac{Z_2}{K_1-1} + \frac{Z_1}{K_2-1} \tag{17}$$

In calculating K_2, $\gamma_2(x_1)$ can be taken as 1.00 for very dilute solutions.) Repeat steps 5 to 7 until ϕ from Eq. 16 matches the assumed value.

(8) Check the value of x_1 with Eq. 1. Repeat steps 3 to 6 until values of ϕ, x_1, and Z_1 satisfy all the equations. Do steps 3 to 8 for all experimental points.

(9) From the new set of $x_1-(-\Delta T)$ for all measured points, redetermine γ_1^∞ from the improved $[(\partial T)/(\partial x_1)^\infty]$ until convergence for γ_1^∞ is found.

Calculations using the superheat temperature T_s

From the superheat temperature for pure ethyl acetate ($T_s = 48.3475°\text{C} = 321.498$ K) $p_s = 35.520$ kPa, giving (Eq. 10)

$$p_s - p = 35.520 - 33.549 = \rho g \Delta Z_{\text{eff}} = 8.4672 \Delta Z_{\text{eff}}$$

$$\text{and} \quad \Delta Z_{\text{eff}} = 0.2327 \text{ m } \left(\rho = 0.864 \text{ g/cm}^3\right).$$

Using the same calculation procedure as for the n-hexane–ethanol system given earlier, one obtains, for example, for point 2, using $x_1 = 0.0050$

$$x_1' = 0.00504$$
$$A = -0.00266$$
$$B = 0.9999.$$

And finally,

$$\phi = \frac{(181.25)(1.4032) - 0.00266\lambda_S}{\lambda_S - 0.999\lambda_T}.$$

For latent heats $\lambda_T =$ 34,328.8 and $\lambda_S = 34{,}237.9$ J/kg,

$$\phi = 1.731 \text{ (clearly incorrect)}.$$

Again the calculations are extremely sensitive to the value of ΔZ_{eff} and the correct value is obtained for $\Delta Z_{\text{eff}} = 0.2337$.

Also for points 1 and 3, ϕ values close to those found in Table 2 are obtained with $\Delta Z_{\text{eff}} = 0.2339$ and $\Delta Z_{\text{eff}} = 0.2337$, respectively.

Equation 7 permits evaluation of (m_2/F) and the ratio $(m_2/F)/\phi$, information not accessible by other means. The results, based on the corrected values for ΔZ_{eff}, are shown in Table 3. The results indicate that between 68 and 76% of the eventual vaporization already takes place at or before the entrance to the Cottrell pump. For the n-hexane–ethanol system the corresponding figure is about 89%.

Discussion and Conclusion

Two procedures have been developed and demonstrated for determining the important but elusive vaporization ratio (ϕ) in a differential ebulliometer. Previous attempts by sev-

Table 2. Ebulliometric Data for the n-Hexane (1) – Ethyl Acetate (2) System

x_{s1}	T (K)	T_s (K)	x_1	Z_1	ϕ	P_Σ (kPa)
0	320.0943	321.4975	—	0	—	—
0.003603	319.854	321.2572	0.00310	0.003364	0.0280	33.539
0.005804	319.684	321.0872	0.0050	0.005424	0.0290	33.498
0.008402	319.4555	320.8587	0.0073	0.00787	0.0264	33.646

Source: Bedassi (2001).
Note: System pressure = 33.549 kPa.

Table 3. Calculated Dimensionless Quantities Based on Superheat Temperatures and Corrected Values for ΔZ_{eff}

x_{s1}	x_1	x'_1	$-A$	B	ϕ	m_2/F
0.003603	0.0031	0.003167	0.0070	0.9866	0.0269	0.0195
0.005804	0.0050	0.005106	0.00695	0.9870	0.0307	0.0234
0.008402	0.0073	0.007455	0.00706	0.9870	0.0237	0.0163

Note: n-Hexane (1)−Ethyl Acetate (2) at $P = 33.549$ kPa.

eral authors to find ϕ for a specific system and operating conditions contained varying approximations and have not been too successful. The first method is a trial-and-error procedure in which all three equations governing an ebulliometer operation are satisfied. Although fairly extensive computation is required, the procedure is considered the most reliable yet. In addition to the $\Delta T - x_{s1}$ measured data, it requires only the pure-component vapor pressures and the dimensionless reboiler and vapor holdup quantities (R'/S') and (V'/S'). Once determined, these should remain essentially constant from one system to another at low pressures (<1 bar), if the equipment is filled with the same *volume* of charge.

The second procedure requires measurement of the superheat temperature, T_s, at the base of the Cottrell pump, and physical properties in the form of liquid heat capacity and latent heats of vaporization. The procedure rests on the major assumption that at the base of the Cottrell pump where the temperature, T_s, is measured, a local vapor−liquid equilibrium is established, that is, that the measured or calculated pressure, P_s, is in accordance with

$$P_s = \Sigma x_i \gamma_i \, p_i^{\mathrm{sat}}.$$

Vigorous mechanical stirring in the reboiler (as done in our apparatus) will promote this equilibration and also assists in producing smooth boiling and temperature stability.

The calculation of ϕ forms only part of the larger iterative calculation procedure for finding γ_1^{∞} in an ebulliometer that has been characterized according to Eq. 1. A disadvantage of the procedure is its marked sensitivity to the effective hydrostatic head $\rho g \Delta Z_{\mathrm{eff}}$ in particular, and also to measured temperatures and pressures. This sensitivity should decrease with systems or conditions that have a larger vaporization ratio, ϕ. The data used in the sample calculations were obtained with pressure control by a commercial pressure controller. For the systems studied, n-hexane (1)−ethanol (2) and n-hexane (1)−ethyl acetate (2), a more sophisticated PC-based control system such as used by Joseph et al. (2001) for a dynamic VLE apparatus is desirable. To confirm the general validity of this procedure for finding ϕ, more extensive measurements for a variety of systems will be needed with the most precise pressure control possible. Such a control system is now being implemented for our ebulliometers.

If a correlation in terms of measurable quantities (such as the numerator in Eq. 9) can be found relating the vaporization ratios (m_2/F) and ϕ (at the entrance and discharge ends of the Cottrell pump), Eq. 4 will provide a rigorous and direct trial-free method for finding ϕ. (It has been found that (m_2F) can be eliminated from Eq. 4 by measuring T and T_s at two or more slightly increased pressures for the pore solvent, assuming (m_2/F) to remain constant. The ϕ values so obtained (by subtraction) will have error (since m_2/F is not constant), but can be linearly extrapolated to zero temperature difference, giving, for example, $\phi = 0.045$ for pure ethanol.) For the n-hexane−ethyl acetate system, the ratio (m_2/F) is nearly constant at about 0.724, whereas for the n-hexane−ethanol system a ratio of 0.89 was found.

Finally, an interesting consideration arises in connection with the derivation of Eq. 1. In the derivation (Raal, 2000) it was assumed that the overall composition in the reboiler is the same as that circulating in the Cottrell pump, Z_i. This would be true if the Cottrell pump acts as a purely mechanical pump, transporting the incoming liquid without overall composition change. At the other extreme, if the reboiler produces and transports only vapor (as in an Othmer-type VLE still), the reboiler composition would differ considerably from that of the rising vapor. A more general derivation can thus be made in which the overall composition of the reboiler at equilibrium, Z_{Ri}, may differ from Z_i. The derivation, similar to that of Raal (2000), is lengthy but can be cast in the form

$$x_1 = \frac{x_{s1}}{1 + (K_1 - 1)E + \left(\frac{R'}{S'}\right)\left(\frac{Z_{R1} - Z_1}{x_1}\right)} \tag{18}$$

Evaluation of the correction term in the denominator of Eq. (18) is difficult, but estimates from our data suggest that it is sufficiently small to be neglected for practical purposes in calculating x_1 from the charge composition, x_{s1}. If the vapor and liquid compositions in the reboiler are the same as those at the entrance to the Cottrell pump (y'_1, x'_1) the *overall* composition difference $(Z_{R1} - Z_1)$ can still be nonzero if the evaporation ratio m_2/F differs from the static holdup ratio of vapor to liquid in the reboiler, as shown by Eq. 19 below:

$$(Z_1 - Z_{R1}) = x'_1(K'_1 - 1)\left\{m_2/F - \frac{V'_R}{R'}\right\}. \tag{19}$$

Notation

A = dimensionless concentration ratio, as defined in Eq. 7, or constant in Margules equation, Eq. 13
B = dimensionless concentration ratio, as defined in Eq. 7
Cp_L = liquid heat capacity, J/kgK
E = ebulliometer parameter as in Eq. 1a
F = molar flow rate of fluid in Cottrell pump
$f = V/L = \phi/(1 - \phi)$
g = gravitational acceleration, m/s^2
H, h = vapor, liquid, or overall stream enthalpy, J/mole
K_i = equilibrium constant, y_i/x_i at temperature, T
K'_i = equilibrium constant, y'_i/x'_i, at temperature, T_s
L = liquid molar flow rate, moles/s
M = molecular mass
$\dot{m}$ = mass-flow rate
m_2 = vapor molar flow rate at entrance to Cottrell tube
P = system pressure, kPa
$P_\Sigma = \Sigma x_i \gamma_i p_i^{\mathrm{sat}}$
p_i^{sat} = pure-component vapor pressure, kPa
p_s = pressure where T_s is measured, for example, at Cottrell pump entrance, kPa
R' = molar "static" holdup in reboiler
S' = molar charge in ebulliometer

T = equilibrium temperature, K
T_s = measured temperature at entrance to Cottrell tube, K
V = vapor molar flow rate
V' = molar vapor "static" holdup
x_i = equilibrium liquid mole fraction
x'_i = equilibrium liquid mole fraction at T_s and p_s
x_{s1} = charge composition, mole fraction
y_i = equilibrium vapor mole fraction
y'_i = value of y_i at T_s, p_s
ΔZ = height of liquid column, m
ΔZ_{eff} = effective height, as reflected by pressure, p_s, m
Z_{R1} = reboiler composition if different from Z_1 (Eq. 18)

Greek letters

λ_T, λ_s = molar latent heats at temperatures T, T_s
ϕ = molar flow-rate ratio, V/F
ρ = liquid density, kg/m^3
Φ_i = correction factor in activity-coefficient equation

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