Characterization of Differential Ebulliometers for Measuring Activity Coefficients

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Differential ebulliometry is a powerful and rapid procedure for obtaining infinitely dilute activity coefficients with potentially very good accuracy. Tedious degassing procedures are not necessary, as in a static method, and from only a few measurements full system phase behavior can be evaluated. The principal problem, precise evaluation of the equilibrium liquid composition from the known composition of a prepared solution charged to the apparatus, is well known but has so far defied adequate resolution. A system of exact self-consistent equations was developed for the characterization of an ebulliometer through a dimensionless ebulliometer constant. Evaluation of this constant from typical data and its subsequent use are illustrated for a system of known phase equilibrium behavior. Remarkably, the equations permit evaluation of the effective "static" holdups in various parts of the equipment without any volume measurements. Since one equation is redundant to the main purpose, it can be used for a consistency check of measured and calculated data. The equations also furnish a guide for the operation of ebulliometers.

Introduction

The measurement of infinitely dilute activity coefficients has become a very attractive procedure for obtaining phase-equilibrium data rapidly and accurately. The measurement of γ_i^∞ by any one of several methods represents a considerable economy of effort over determination of a full set of VLE data, that is, over the entire composition range. Also the greatest departure from ideality is usually (although not invariably) found in the very dilute regions, and accurate information in these regions is often of considerable practical and theoretical interest. In the limit, γ_i^∞ characterizes the behavior of a single solute molecule completely surrounded by solvent molecules. In many industrial separation operations the system behavior in the very dilute regions becomes crucial in process design for high-purity products, frequently the most difficult or expensive part of a separation.

There are basically four experimental procedures for obtaining infinitely dilute activity coefficients, viz.:

- By differential ebulliometry
- By use of a differential static apparatus
- By gas chromatographic methods
- By inert gas stripping.

Raal and Mühlbauer (1998) have briefly reviewed these four methods. An additional procedure, involving measurement of molar refraction, has recently been used (Dutt and Prasad, 1989), but has received little attention. A dew-point measuring procedure has also been demonstrated by Suleiman and Eckert (1994).

Differential ebulliometry and the static differential method (where total pressure changes with solute concentration are measured at constant temperature) have received much coverage in the literature, with studies, for example, by Olson (1989), Lobien and Prausnitz (1982), Dallinga et al. (1993), Dohnal and Novotna (1985), Eckert et al. (1981), Trampe and Eckert (1990), Delcros et al. (1995), Alessi et al. (1986) among others. An interesting earlier review of ebulliometry was given by Ambrose (1975) with attention to superheating, ebulliometer design, radiative effects, and the possible influence of any gas–vapor interface.

For systems involving a heavy (comparatively nonvolatile) component, GC techniques become attractive, but the inability of the technique, in its typical use, to furnish information on γ^∞ for the heavy solvent is a drawback. UNIFAC interaction parameters can, however, be found by GLC methods by producing data sets in which the functional group of interest appears in both solute and solvent molecules, as demonstrated, for example, by Alessi et al. (1982).

The gas stripping method, also referred to as the exponential dilutor method, has more recently found favor for systems of high relative volatility, for example, Wobst et al. (1992) and Hradetzky et al. (1990).

Differential ebulliometry and the differential static method are arguably the most popular procedures for obtaining γ_i^∞ for both solute and solvent and it is the purpose of this publication to derive and analyze a consistent set of equations governing differential ebulliometry. In particular, the principal problem of finding the true equilibrium liquid composition from the gravimetrically prepared charge composition is addressed. Important considerations in making a choice between the differential ebulliometric and static methods are the following:

- In differential ebulliometry equilibrium can be achieved fairly rapidly, and there is no need for troublesome and time-consuming degassing procedures. Temperature changes (with composition) can be measured at least as accurately as differential pressure changes (in the static ebulliometric method).
- A highly invariant temperature environment, for the static method, is probably more easily achieved in practice than a constant pressure, as required for a dynamic ebulliometer.
- The vapor holdup in a static cell is generally negligible except at high pressures and the gravimetrically prepared mixture composition can usually be used directly without any major corrections.
- Static methods are favored for systems of high relative volatility (Olson, 1989).
- In dynamic ebulliometry the liquid becomes superheated at or before the entrance to the vapor-lift pump, and this may lead to "bumping" and temperature fluctuations. Energy input should be such that small increases or decreases should not affect the observed temperature. The superheat should be fully discharged where the liquid−vapor mixture impinges on the temperature sensor. For certain classes of pure fluids there is no "plateau region" in which the boiling temperature remains invariant when energy input to the boiler is increased. As noted by Kneisl et al. (1989), this is a serious problem (not related to product purity), since boiling points cannot then be accurately determined. Poorly behaved fluids, characterized by a plateau region with slopes exceeding 300 μKW^{-1}, were classified according to their dipole moments and a parameter reflecting the extent and type of molecular association. Liquids that become highly superheated may not fully discharge their superheat in the thermowell area, that is, the temperature rise due to superheat may not be balanced by evaporative cooling. A two-element thermowell design is being studied in our laboratory in which the principal superheat-discharge element is insulated thermally from the temperature-sensing element. Rapid stirring in the boiling chamber is advisable for all classes of fluids.
- There is some question as to whether a dynamic equilibrium, as achieved in a dynamic VLE still or ebulliometer, is fully equivalent to the static equilibrium achieved in an isothermal stirred static cell. In practice this possible difference is generally considered negligible.

In an ebulliometer the solvent must be of the highest purity since any impurity will compete in its influence with the solute. The true mole fraction of impurity, as distinct from the claims of the supplier, can be found by determining response factor ratios (Raal and Mühlbauer, 1998).

The rapidity with which measurements can be made in ebulliometry is due in a large part to the fact that a gravimetrically prepared mixture (of very accurately known composition) can be used and that, in a typical procedure, no composition analyses are required, except perhaps to test the purity of the solutes and solvents by GC analysis. A troublesome aspect of dynamic ebulliometry is that the *prepared* solution composition is not the same as that of the equilibrium liquid that separates from the vapor in the thermowell area. Nor is it the same as the overall composition of the vapor−liquid mixture in the vapor-lift pump. To obtain the limiting activity coefficients, γ_i^∞, a plot of the temperature difference between the boiling point of the solvent and that of a dilute solution is required as a function of the *equilibrium* liquid composition. The equations of Gautreaux and Coates (1955) or other more recent versions accounting for vapor-phase nonidealities may then be used to find γ_i^∞. The static holdup of vapor and liquid has been accounted for by Dohnal and Novotna (1985), to produce an equation for calculating γ_i^∞ from the measured scope $(\partial T/\partial x_1)_p^\infty$. This equation contains *three* quantities, all difficult to assess, viz., the "evaporation ratio" f, which is the ratio of vapor-to-liquid *flows* emerging from the equilibrium chamber (that is, V/L), and the static holdups N_V and N_L (in their nomenclature). The latter two quantities are dependent on the equipment construction and on the total moles of material charged to the apparatus and are exceedingly difficult to measure accurately.

Presented below is a rigorous analysis of ebulliometer operation in such a way that a true ebulliometer "constant," or parameter that characterizes the instrument, can be obtained and evaluated. Remarkably, it was found that the static holdups of both the liquid and vapor could be found without any volume measurements. Moreover, the dynamic vaporization ratio $f(=V/L)$ is also determined. For the complete characterization, that is, to determine all equipment constants, two equilibrium measurements at different vaporization ratios are required for a system of known phase behavior. For the apparatus characterization (only), it is necessary to measure either the equilibrium liquid composition x_i, for example, in an ebulliometer where vapor and liquid streams are fully separated (see Figure 1), or the composition Z_i of the recombined vapor/liquid stream returned to the boiling chamber as in Figure 2. In an ebulliometer apparatus consisting of, say, four similar ebuliometers connected to a common pressure manifold, a sample septum point need only be installed into one of the ebulliometers to permit characterizing for all the (similar) units. For ebulliometer constant E (see below) to be valid, that is, unchanged for a new system of unknown phase equilibrium behavior, it is necessary that the fractional vapor flow rate V/F $(=\phi)$ be maintained constant, as will be seen from the analysis below. The dynamic ratios f and ϕ are simply related by the material balance for a flash vaporization operation, that is, $\phi = f/(f+1)$.

The three separate ebulliometer parameters, as used by Dohnal and Novotna (1985) and subsequently by others (such as Delcros et al., 1995; Vrbka and Dohnal, 1992, are combined into a single dimensionless characterizing parameter E. The application of the procedure is illustrated with an example. The importance of static liquid and vapor holdup has

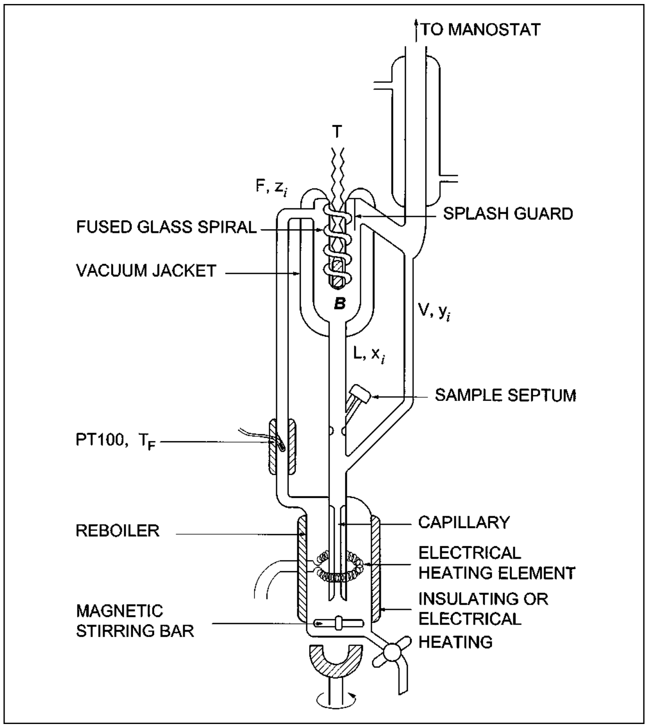

Figure 1. Ebulliometer with separation of equilibrium liquid and vapor streams.

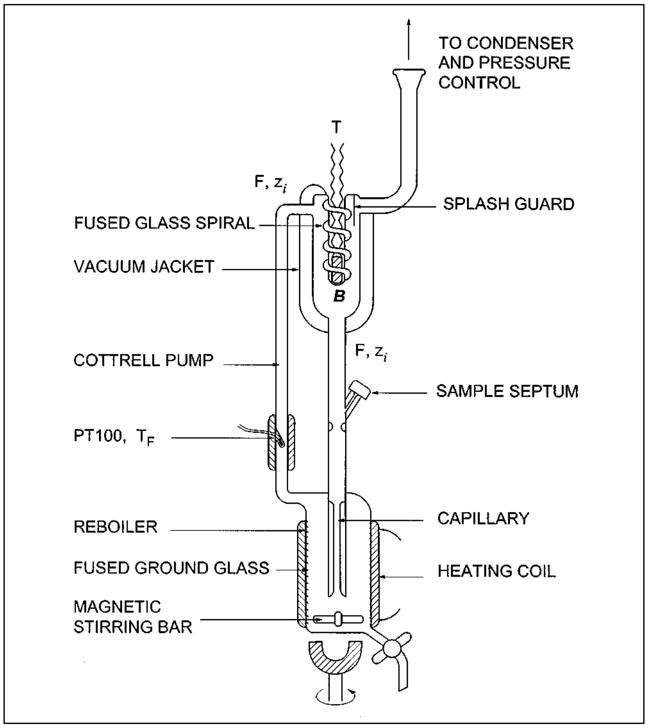

Figure 2. Ebulliometer with no separation of equilibrium liquid and vapor streams.

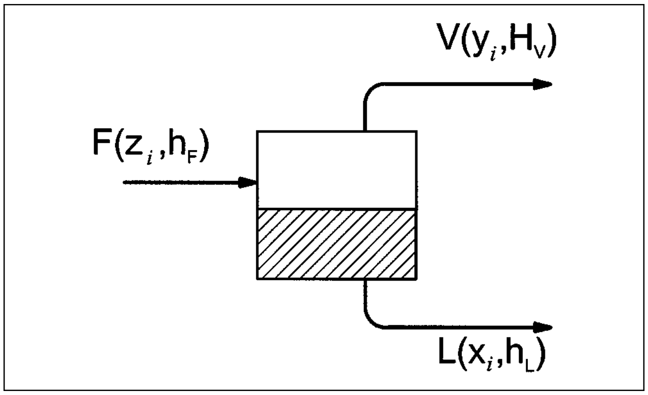

Figure 3. Equilibrium flash unit.

been recognized by other researchers, for example, Trampe and Eckert (1990) and Eckert et al. (1981), who made experimental measurements of holdup volumes, and Dallinga et al. (1993), Goncalves and Macedo (1993), Olson (1989), and Pividal et al. (1992).

Analysis

Dynamic flow analysis

Two types of ebulliometer are shown in Figures 1 and 2. In the design of Figure 1, vapor and liquid streams are fully separated before recombination above the boiling chamber *R*. In the simpler design of Figure 2 (as used by Thomas et al., 1982, for example) there are no separate equilibrium vapor- and liquid-stream paths. The analysis below applies to both examples. In the second design, favored because of its simplicity, only the combined liquid- and vapor-stream composition, Z_i, can be measured, for example, by installing a sample septum in the downcomer before it reenters the reboiler, as shown. This is only for characterization purposes. In the design of Figure 1, the equilibrium liquid composition, x_i, can similarly be measured.

The upper portion of an ebulliometer, *B*, is an adiabatic flash chamber, where superheat is discharged. The analysis for a flash chamber, Figure 3, is as follows:

$$F = V + L \tag{1}$$

$$FZ_i = Vy_i + Lx_i. \tag{2}$$

From Eq. 2,

$$V\left(\frac{y_i}{x_i}\right)x_i + Lx_i = FZ_i.$$

In terms of the equilibrium constant $K_i(= y_i/x_i)$, and solving for x_i, this becomes

$$x_i = \frac{Z_i}{\dfrac{K_iV}{L+V} + \dfrac{L}{L+V}}$$

and, with $f = V/L$,

$$x_i = \frac{Z_i(1+f)}{1+K_if}. \tag{3}$$

When the equilibrium constant is known, f can be found in terms of K_i and Z_i. A convenient relationship is that of Rachford and Rice as given in King (1971), in terms of the *bounded* variable $\phi(=V/F)$, where $\phi = f/(1+f)$. For a multicomponent system:

$$\sum_{i=1}^{m} \frac{Z_i(K_i-1)}{(K_i-1)\phi+1} = 0. \tag{4}$$

Since we are dealing only with binaries,

$$\frac{Z_1(K_1-1)}{(K_1-1)\phi+1} = -\frac{Z_2(K_2-1)}{(K_2-1)\phi+1}.$$

Solving for ϕ gives

$$-\phi = \frac{Z_2}{K_1-1} + \frac{Z_1}{K_2-1}. \tag{5}$$

Equation 5 plays an important part in finding ϕ from measured data.

Principal ebulliometer equation

Consider now the distribution of the total charge S' (moles) between the reboiler (R') and static liquid and vapor holdup quantities, L' and V'. Quantities R', L', and V' are dependent on the equipment construction and on the total charge introduced into the ebulliometer and, as just mentioned, very difficult to determine experimentally:

$$L' + V' + R' = S'. \tag{6}$$

For component i of a binary,

$$L'x_i + V'y_i + R'Z_i = S'x_{Si}, \tag{7}$$

that is,

$$L'x_i + V'K_i x_i + R'Z_i = S'x_{Si}. \tag{7a}$$

From Eq. 3, however, x_i and Z_i are related, and the latter can be substituted for in Eq. 7a:

$$L'x_i + V'K_i x_i + R'\left\{\frac{x_i(1+K_i f)}{1+f}\right\} = S'x_{Si}.$$

Dividing by S' and letting $L' = S' - V' - R'$ in the preceding equation gives:

$$x_i\left\{1 - \frac{V'}{S'}(1-K_i) + \frac{R'}{S'}\left(\frac{1+k_i f}{1+f} - 1\right)\right\} = x_{Si}.$$

Further simplification gives

$$x_i\left\{1 - (K_i-1)\left[V'/S' + R'/S'\frac{f}{1+f}\right]\right\} = x_{Si},$$

that is,

$$x_i = \frac{x_{Si}}{1+(K_i-1)E}, \tag{8}$$

where E is the "ebulliometer constant" given by

$$E = V'/S' + (R'/S')\phi. \tag{8a}$$

Evaluation of E thus permits *exact* calculation of the equilibrium liquid concentration x_i, required for the ΔT vs. x_i plot. The experimental determination of E, using a system of known phase equilibrium behavior, is discussed and illustrated below.

In measuring a new system it is clear, however, that a trial-and-error procedure is necessary to obtain γ_i^∞ once E has been determined, since $K_i = (y_i/x_i)$ is not known *a priori*, but depends on γ_i:

$$K_i = \frac{\gamma_i p_i^{\text{sat}}}{P\Phi_i}, \tag{9}$$

where the correction term Φ_i is given by

$$\Phi_i = \frac{\hat{\phi}_i}{\phi_i^{\text{sat}}} \exp\left[-\frac{\upsilon_i^L(P - P_i^{\text{sat}})}{RT}\right]. \tag{9a}$$

At low pressures this correction is frequently negligible. The fugacity terms $\hat{\phi}_i$ and ϕ_i^{sat} and the liquid molar volume υ_i^L are not to be confused with ϕ, ϕ', V, or V' used in other equations earlier. Also, R is the ideal gas constant.

The procedure for obtaining the correct x_i and γ_i from the known x_{Si} (that is, the prepared solution composition) and its corresponding temperature consists of estimating x_1, for example, $x_1^{(1)} = x_{S1}$, for several different concentrations and plotting the measured temperature differences ΔT vs. x_1. From the limiting slope of such a plot the first estimate of γ_1^∞ is obtained from the well-known equations relating $(\partial T/\partial x_1)_p^\infty$, γ_1^∞, and the saturation pressures, p_i^{sat}. A convenient form, with correction for vapor-phase nonideality based on the truncated virial equation, is given by (Dohnal and Novotna, 1985):

$$\gamma_1^\infty = \epsilon_1^\infty P_2^{\text{sat}}\left[1 - \beta\left(\frac{\partial T}{\partial x_1}\right)_p^\infty\right], \tag{10}$$

where

$$\epsilon_1^\infty = \exp\left[(B_{11} - \nu_i^L)(p_2^{\text{sat}} - p_1^{\text{sat}}) + \delta_{12}\, p_2^{\text{sat}}\right]$$

$$\beta = \left(1 + p_2^{\text{sat}}\frac{B_{22} - \nu_i^L}{RT}\right)\frac{d \ln p_2^{\text{sat}}}{dT}$$

$$\delta_{12} = 2B_{12} - B_{11} - B_{22}.$$

The B_{ij} are second virial coefficients, and υ_i^L is the liquid molar volume. A convenient low-pressure simplification of

Eq. 10 is given by

$$\gamma_1^\infty = \frac{p_2^{\text{sat}} - \left(\dfrac{\partial T}{\partial x_1}\right)_p^\infty \dfrac{dp_2^{\text{sat}}}{dT}}{p_1^{\text{sat}}}. \tag{11}$$

The $\gamma_i^{(1)}$ obtained from Eq. 10 or Eq. 11 can then be fitted to a simple one-constant equation such as the Margules symmetric (Porter) equation:

$$\ln\gamma_1 = Ax_2^2 \quad (\ln\gamma_1^\infty = A)$$

to obtain A.

If the system relative volatility is large, a more flexible single-constant equation may be desirable. It is only necessary that the equation be capable of representing γ_1 as a function of x_1 with reasonable accuracy over a very small concentration range, such as $0 < x_1 \leq 0.03$. The K_1 values are then computed for each measured point from Eq. 1, and Eq. 8 then produces improved estimates for the equilibrium liquid compositions x_1.

To find the limiting slope $(\partial T/\partial x_1)_p^\infty$ from a plot of ΔT vs. x_1, relatively simple algebraic expressions such as those recommended by Thomas et al. (1982) can be fitted. If K_1 is neither too large nor very small, the iterative procedure sketched before should converge rapidly. For large K_1 (such as for alcohol-hydrocarbon systems) a more sophisticated iterative or convergence procedure may be required.

The sensitivity of γ_i to errors in the measured temperature gradient can be estimated by differentiating Eq. 11 to give

$$\frac{d\gamma_1^\infty}{d\left(\dfrac{\partial T}{\partial x_1}\right)_p^\infty} = -\frac{p_2^{\text{sat}}}{p_1^{\text{sat}}}\left\{\frac{(K_1^\infty - 1)}{\left(\dfrac{\partial T}{\partial x_1}\right)_p^\infty}\right\}.$$

The greatest sensitivity will be for systems having a large K_1^∞ and for which the solvent is much more volatile than the solute ($p_2^{\text{sat}} \gg p_1^{\text{sat}}$). For such systems very accurate $\Delta T - x_1$ data will be needed to give reliable γ_i^∞ values, as was also pointed out by Eckert et al. (1981).

The dimensionless vapor and reboiler holdups V'/S' and R'/S' should remain constant in any ebulliometer when filled with the same volume of charge. However, E does depend on the *dynamic* quantity ϕ, and for accurate results with different systems or with a given system at different concentrations, the energy input should be such that the fractional vapor production remains constant. For this purpose a drop counter installed at the bottom of the condenser will prove useful. A constant drop rate, however, does not necessarily guarantee a constant ϕ. A more rigorous indication is given by an energy balance around the flash chamber, which it is assumed is thoroughly insulated (that is, adiabatic), as it should be. Neglecting kinetic and potential-energy terms in the macroscopic energy balance gives

$$\Delta H = 0.$$

Thus,

$$Fh_F = VH_V + Lh_L \tag{12}$$

$$\therefore h_F = \left(\frac{V}{F}\right)H_V + \left(\frac{F-V}{F}\right)h_L.$$

In terms of $\phi(=V/F)$,

$$h_F = \phi H_V + (1-\phi)h_L,$$

giving

$$\phi = \frac{h_F - h_L}{H_V - h_L}. \tag{13}$$

Since the solutions are extremely dilute the mixture enthalpies in Eq. 13 can be equated to the pure solvent values, so that $(H_V - h_L)$ equals the solvent latent heat of vaporization, λ_2. The numerator represents the superheat energy discharged and can be approximated by

$$h_f - h_L = Cp_2(T_F - T), \tag{13a}$$

where C_p is the liquid heat capacity of the solvent, and T_F is the temperature of the superheated liquid or liquid/vapor mixture. If the liquid heat capacity is not constant over the temperature interval $T_F - T$, but varies linearly with T, for example,

$$Cp_2 = Cp_2^0 + b(T - T_0)$$

(T_0 is a reference temperature), Eq. 13a becomes for $T_0 = T$ = equilibrium temperature:

$$h_F - h_L = Cp^0(T_F - T) + \frac{b(T_F - T)^2}{2}. \tag{14a}$$

Excess enthalpies do not arise since pure liquids are assumed. Once ϕ has been found for a test system of known phase equilibrium behavior, this factor should be kept as constant as possible for measurements on a new system, for example, by adjusting the energy input so that

$$\phi = Cp_2(T_F - T)/\lambda_2 \tag{14b}$$

or

$$\phi = \left[Cp(T_F - T) = \frac{b}{2}(T_F - T)^2\right]\Big/\lambda_2$$

remains at the previously determined value. Failure to operate with a constant ϕ or to account correctly for the static holdups may be responsible for some of the considerable data discrepancies evident in the literature for systems of large K such as alcohol-hydrocarbon systems. A temperature sensor installed near the base of the Cottrell pump as illustrated in Figures 1 and 2 should permit a satisfactory estimate of the superheated liquid temperature T_F.

Subsidiary equations

Two other important equations can now be derived. The first relates the gravimetrically prepared solution composition x_{Si} to the overall composition of the fluid in the Cottrell pump, Z_i. The second relates x_{Si} and Z_i to the nondimensional holdup in the reboiler, R'/S'. The purpose and use of these two additional equations will be made clear below. Equations 3 and 8 can be combined to eliminate x_1 in favor of Z_1:

$$x_1 = \frac{x_{S1}}{1+(K_1-1)E} \tag{8}$$

and

$$x_1 = \frac{Z_1(1+f)}{1+K_1 f} = Z_1 b, \tag{3}$$

where, for convenience,

$$b = \frac{1+f}{1+K_1 f}.$$

Since $f/(1+f) = \phi$, b can be written more conveniently in terms of ϕ,

$$b = \frac{1+\dfrac{\phi}{1-\phi}}{1+K_1\dfrac{\phi}{1-\phi}} = \left[1+\phi(K_1-1)\right]^{-1}.$$

Therefore, from Eq. 8,

$$x_1 = \frac{Z_1}{1+\phi(K_1-1)},$$

and Eq. 3 becomes

$$x_{S1} = Z_1\left\{\frac{1+(K_1-1)E}{1+(K_1-1)\phi}\right\}. \tag{15}$$

Since both x_{S1} and Z_1 will be known in a characterizing experiment, Eq. 15 permits calculation of E when ϕ is known.

The equation relating x_{Si}, Z_i, and R'/S' derived in the Appendix, is as follows:

$$R'/S' = \frac{x_{S1}+D'}{Z_1+D'}, \tag{16}$$

where

$$D' = \left(\frac{K_2-1}{K_1-K_2}\right)\left\{\frac{1+K_1 f'}{1+f'}\right\}. \tag{16a}$$

Equation 16 is not *necessary* for characterization of an ebulliometer, since Eq. 8 alone will suffice, so it can thus serve as a consistency check on measured and calculated quantities. Since Eq. 16 does not contain the dynamic quantity ϕ, it is valid for all circulation rates. The system of four equations, Eqs. 5, 8, 15 and 16, form a consistent set governing and constraining the various compositions present in an ebulliometer. For convenient reference they are given in Table 1, where subscript 1 is the solute and subscript 2 is the solvent.

Table 1. Ebulliometry Equations

$$-\phi = \frac{Z_2}{K_1-1} + \frac{Z_1}{K_2-1} \tag{5}$$

$$x_1 = \frac{x_{S1}}{1+(K_1-1)E} \tag{8}$$

where

$$E = (V'/S') + (R'/S')\phi \tag{8a}$$

$$x_{S1} = Z_1\left\{\frac{1+(K_1-1)E}{1+(K_1-1)\phi}\right\} \tag{15}$$

$$R'/S' = \frac{x_{S1}+D'}{Z_1+D'} \tag{20}$$

where

$$D' = \frac{(K_2-1)}{(K_1-K_2)}\left\{\frac{1+K_1 f'}{1+f'}\right\} \tag{20a}$$

In all the equations in the table, primes denote “static” holdup quantities, while the nonprimed symbols, V, L, f, and ϕ, for example, are molar flow rates or flow-rate ratios.

Illustrative example

Characterization of an ebulliometer requires modification of its design so that either the equilibrium liquid composition x_1 or the combined liquid–vapor composition Z_1 can be measured together with the equilibrium temperature, as discussed earlier. Our recently developed ebulliometers do not have this modification and actual $(T - x_{Si} - Z_i)$ data are not yet available. The use of the equation set can, however, be illustrated for a system of known phase equilibrium properties. For the system *n*-hexane(1) as solute and ethyl acetate (2) as solvent, γ_i^∞ data are available for both ends of the composition range, that is, γ_1^∞ and γ_2^∞ (Thomas et al., 1982). At 340 K, for example, by interpolation from data at other temperatures, we have

$$\gamma_1^\infty = 2.52, \qquad \gamma_2^\infty = 2.38.$$

Pure-component vapor pressures are given in torr units by (Reid et al., 1977):

$$\ln p_1^{\mathrm{sat}} = 15.8366 - \frac{2{,}697.55}{T(\mathrm{K}) - 48.78}$$

$$\ln p_2^{\mathrm{sat}} = 16.1516 - \frac{2{,}790.5}{T(\mathrm{K}) - 57.15}.$$

Suppose measurements at 340 K in an ebulliometer, such as in Figure 2, gave the following values in mole fractions at a total pressure of 74.018 kPa:

$$x_{S1} = 0.01888 \text{ (prepared solution)}$$

$$Z_1 = 0.01823 \text{ (liquid + vapor composition)}.$$

Suppose also for illustrative purposes that the 3 suffix Margules equations with temperature-independent constants can describe the system in the dilute region:

$$\ln \gamma_1 = x_2^2\{A_{12} + 2(A_{21} - A_{12})x_1\} \tag{17}$$

$$\ln \gamma_2 = x_1^2\{A_{21} + 2(A_{12} - A_{21})x_2\} \tag{18}$$

$$A_{12} = \ln \gamma_1^{\infty} = 0.92426, \qquad A_{21} = \ln \gamma_2^{\infty} = 0.86710.$$

Determination of ebulliometer constant E and liquid composition x_1

The following iterative sequence was found satisfactory:

1. Estimate x_1 as $x_1^{(1)} = Z_1 = 0.01823$; also $x_2 = Z_2 = 1 - Z_1 = 0.98177$.
2. From the Margules equations, $\gamma_1^{(1)} = 2.442$, $\gamma_2^{(1)} = 1.00032$.
3. $K_1^{(1)} = (\gamma_1^{(1)} p_1^{\text{sat}})/P = 3.1485$ (taking $\Phi_i = 1$ for convenience)

$$K_2^{(1)} = \frac{\gamma_2^{(1)} p_2^{sat}}{P} = 0.96725.$$

4. Estimate ϕ from Eq. 5

$$-\phi = \frac{Z_2}{K_1^{(1)} - 1} + \frac{Z_1}{K_2^{(1)} - 1} = -0.09935$$

$$\phi^{(1)} = 0.09935.$$

5. Estimate E from Eq. 15, solved for E:

$$E^{(1)} = \frac{\dfrac{x_{S1}}{Z_1}\left\{1 + (K_1 - 1)\phi^{(1)}\right\} - 1}{K_1 - 1}.$$

6. Recalculate x_1 from Eq. 8

$$x_1^{(2)} = \frac{x_{S1}}{1 + (K_1 - 1)E^{(1)}} = 0.01502.$$

7. The γ_i and K_i can now be recalculated from the Margules equations and the expressions for K_i in terms of γ_i. The results are

$$\gamma_1^{(2)} = 2.4475$$

$$\gamma_2^{(2)} = 1.00022.$$

The corresponding new K_i are

$$K_1^{(2)} = 3.1556$$

$$K_2^{(2)} = 0.96718.$$

8. Check the previous value of $\phi(\phi = 0.09935)$ using Eq. 5 and the new estimates of K_i,

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

to give

$$\phi^{(2)} = 0.09995.$$

This should be very close to the fully converged value.

9. A further refinement for the estimated E and x_1 gives

$$E^{(2)} = \frac{\dfrac{x_{S1}}{Z_1}\{1 + (K_1 - 1)\phi\} - 1}{(K_1 - 1)}$$

$$= 0.12005.$$

From Eq. 8,

$$x_1 = \frac{x_{S1}}{1 + (K_1 - 1)E} = 0.01500 \text{ (accept)}.$$

This value may be accepted as the converged value for x_1 as required for the ΔT vs. x_1 plot, and the set $x_1 = 0.01500$, $E = 0.1201$ represents a calibration of the ebulliometer for operation at a constant fractional evaporation ratio of ϕ $(= V/F) = 0.09995 \sim 0.100$. This ratio is rather high and probably unrealistic. It corresponds to a superheat of ~17°C according to Eq. 14, and would require a rather large energy input to the reboiler. Values of ϕ of the order of 0.02−0.05 would be more realistic.

The preceding trial-and-error calculations, produced on a handheld calculator, may have produced small inaccuracies.

Calculation of x_1 when E is known

Suppose addition of a known small amount of *n*-hexane to the ebulliometer in the previous example produces the following new data set when operated with a constant value for $\phi(= 0.10)$ and $P = 74.018$ kPa:

$$T = 339.54 \text{ K}, \qquad x_{S1} = 0.02831, \qquad Z_1 = 0.02737.$$

With E and ϕ now known at 0.1200 and 0.100, respectively, a new converged value for x_1 is readily computed by the steps:

1. Estimate $x_1^{(1)} = Z_1 = 0.02737$.
2. Calculate $\gamma_i^{(1)}$ from the Margules equations and hence K_i from

$$K_i = \gamma_i p_i^{\text{sat}}/P \quad [P = \text{constant}].$$

3. Calculate an improved x_1 from Eq. 8,

$$x_1^{(2)} = \frac{x_{S1}}{1 + (K_1 - 1)E}.$$

4. Recalculate γ_i, K_i, and x_i as in steps 2 and 3.

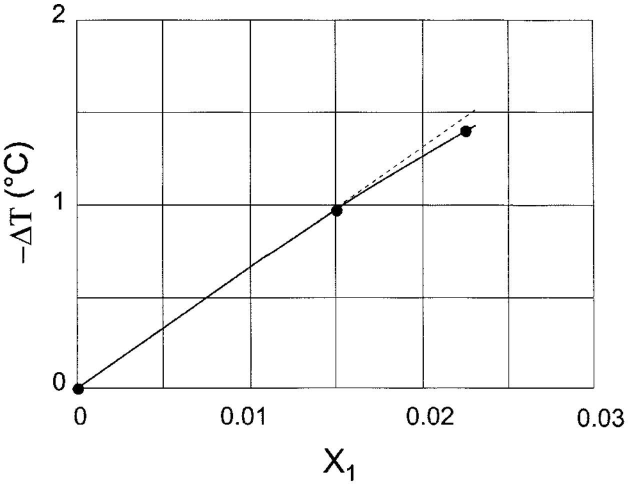

Figure 4. ΔT vs. x_1 plot for determination of γ_1^∞.

Final converged values are as follows:

$$x_1 = 0.02269, \quad K_1 = 3.06423, \quad K_2 = 0.95203$$

$$\gamma_1 = 2.41168, \quad \gamma_2 = 1.00050.$$

The temperature $T = 339.54$ is in accordance with Eq. 11 if the known literature value for γ_1^∞ (2.52) is substituted to give $(\partial T/\partial x_1)_p^\infty = -67.666$ K/mole fraction. The ΔT vs. x_1 values from the preceding two examples are plotted in Figure 4.

Determination of Static Holdup Quantities R'/S', V'/S', and ϕ'

Inspection of Eq. 8 suggests a simple method for determining all the effective static holdup quantities in an ebulliometer *without any volume measurements*. If a second experimental run is made with the same system (of known phase equilibrium behavior) at the same total pressure but at a different vaporization ratio $\phi(=V/F)$, a plot of E vs. ϕ will yield R'/S' and V'/S' as the slope and intercept, respectively. Once R'/S' and V'/S' are known, the remaining static holdup quantity $\phi(=V'/F')$ or $f'(=V'/L' = \phi'/1-\phi')$ is readily determined from the material balance of Eq. 6, which gives

$$V'/S' = \phi'\{1 - R'/S'\} = \frac{f'}{1+f'}\{1 - R'/S'\}. \tag{19}$$

Illustrative example

Suppose, for the *n*-hexane(1)-ethyl acetate(2) system the energy input to the reboiler is reduced from that used for the two previous examples to give a lower vaporization ratio ϕ at the same total pressure. In the characterization of an ebulliometer it is, in any case, desirable to do a few experiments at different ϕ ratios. Suppose the following data are obtained, $x_{S1} = 0.01793$, $Z_1 = 0.01694$, and $T = 340$ K. The iterative procedure used in the first illustrative example rapidly converges to give $E = 0.09089$, $\phi = 0.06022$, and $x_1 = 0.01500$.

A plot of the two E vs. ϕ data points then gives Figure 5, from which $R'/S' = 0.7352$, $V'/S' = 0.0466$, $f' = 0.2137(\equiv \phi' = 0.1761)$.

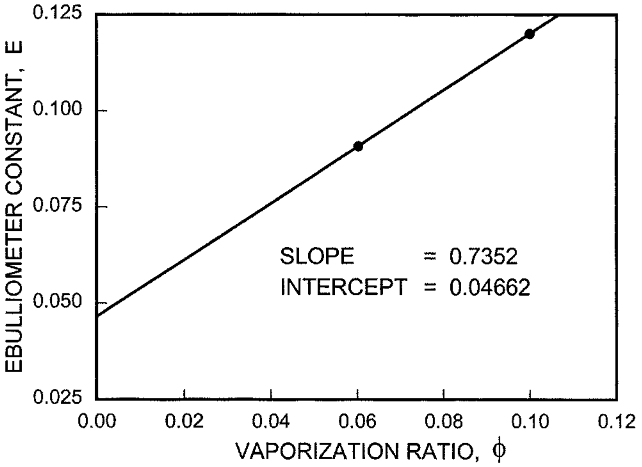

Figure 5. Ebulliometer constant E as a function of vaporization ratio $\phi(=V/F)$.

Note that the static holdups V'/S', R'/S', and L'/S' are the effective holdups under operating conditions. The exact location of liquid or vapor holdups in the equipment need not be specified. The errors in x_1 and E to be expected, if the ebulliometer is operated with a fractional vapor rate ϕ differing from that (0.10) for which the constant E was obtained in the first example, are shown in Table 2.

Computations from Actual Ebulliometer Data

Few data sets in the literature contain sufficient information to permit application of the proposed set of equations. One such example, however, is the data of Eckert et al. (1981), in which measured holdup volumes for vapor and liquid are given, together with the measured temperature rises for the toluene(1)-ethanol(2) system. When converted to dimensionless molar holdup quantities, one obtains $R'/S' = 0.9702$, $V'/S' = 0.00116$, and $V'/L'(=f') = 0.0404$. Computations consistent with Eqs. 5, 8, and 15 gave the results shown in Table 3 for data points 2 and 6 (selected arbitrarily). As for the previous illustrations, the 3-suffix Margules equation were used, with the constants determined from $\gamma_1^\infty = 5.60$, $\gamma_2^\infty = 9.838$ (interpolated to the experimental temperatures), the latter as given in Thomas et al. (1982). Of particular interest in Table 2 are the nonconstant values for E and ϕ. These produce equilibrium liquid compositions x_1 that differ from those calculated by Eckert et al. (1981) from the same holdup data. A test of the consistency of the calculated data in the

Table 2. Error in x_1 and E If the Ebulliometer Is Operated with a Fractional Vapor Rate ϕ Differing from that (0.10) for Which the Ebulliometer Constant E was Obtained

$V'/S' = 0.0467$, $R'/S' = 0.733$, $x_{S1} = 0.01888$						
K_1	ϕ	Error in ϕ (%)	E	Error in E (%)	x_1	Error in x_1 (%)
3.1556	0.100	0	0.1200	0	0.0150	0
3.1556	0.120	20	0.1347	12.3	0.01463	−2.45
3.1556	0.150	50	0.1567	30.6	0.01411	−5.9
3.1556	0.050	−50	0.0834	−30.5	0.0160	6.7
3.1556	0.03	−70	0.687	−40.6	0.0164	9.6

Table 3. Computations from the Ebulliometry Data of Eckert et al. for the Toluene(1)-Ethanol(2) System

	Eckert et al. Data		Calculated to Conform with Eqs. 5, 8, and 15	
	Data Point 2	Data Point 6	Data Point 2	Data Point 6
T(K)	318.266	317.801	318.266	317.801
x_{S1}	0.00940	0.02988	0.00940	0.02988
x_1	0.00905	0.02897	0.00891	0.02786
Z_1	—	—	0.00940	0.02990
f'	0.0404	0.0404	0.0404	0.0404
ϕ	—	—	0.0414	0.0623
E	—	—	0.0413	0.0616
f	—	—	0.0432	0.0657

last two columns is that, when substituted into Eq. 16, they should reproduce the correct value for R'/S', viz., 0.9702. The values obtained for the two data sets were 0.967 and 0.9704, respectively. These are quite satisfactory, since Eq. 16 is very sensitive to small errors in K_i or Z_i, and the two calculated data sets are thus self-consistent. It cannot be stated with certainty that the x_1 values (0.00891 and 0.02786) are correct, and those of Eckert et al. (1981) are inaccurate, unless it can be shown that the Margules equations give an accurate description of the toluene-ethanol system in the very toluene-dilute region.

Discussion and Conclusion

The set of equations presented (Eqs. 5, 8, 15 and 16) relate the prepared solution concentration x_{S1} to the equilibrium liquid composition x_1 and the combined liquid–vapor stream overall composition Z_1 in a rigorous manner. In particular a dimensionless ebulliometer constant E is defined that permits precise characterization of the equipment. If the vaporization ratio ϕ is kept constant when a new system is investigated, it is shown that E must remain constant. To keep ϕ at the same value for a new system the latent heat of vaporization and liquid heat capacity must be known to permit use of Eq. 14 or 14a. As a check, a drop counter in the condenser is useful, particularly to ensure similar operation for all units in a multiunit apparatus. The procedure for determining E, using a system of known phase equilibrium behavior, has been demonstrated for a real system and involves measurement of the composition Z_1 for a single run for one unit of a multiunit apparatus connected to a common manifold. For the examples shown the iterative scheme used converged rapidly to give both ϕ and the true liquid equilibrium composition x_1. When used with data from two runs at different vaporization ratios, ϕ, Eq. 8 surprisingly permits determination of the effective dimensionless static holdups R'/S', V'/S', and V'/L'. This information is useful but not *required* for operation of the ebulliometer.

If the static holdup is not taken into account and the equilibrium liquid composition (x_1) is taken to be that of the prepared solution (x_{S1}) the error in x_1 is proportional to ($K_1 -$ 1). This is in agreement with the findings of Dohnal and Novotna (1985), who showed, by a different route, that the error in the measured γ_1^∞ is proportional to $\alpha - 1$, where $\alpha =$ relative volatility. Since $\alpha = (K_1 - 1)/y_2 \sim (K_1 - 1)$ for very dilute solutions for which $y_2 \sim 1$, the findings are equivalent.

The actual error in x_1 when taken as x_{S1} is easily found from Eq. 8, and for the two examples illustrated amounts to 25.9% and 24.8% respectively. For systems of high relative volatility the error clearly will be much higher and failure to account accurately for the static holdup or operation with a nonconstant ϕ may be the cause of many large discrepancies in data reported in the literature. It can be concluded that the most reliable γ_i^∞ ebulliometry data reported for systems of appreciable relative volatility are those measured by the static differential method, where static holdup of the vapor phase may be negligible. An example of careful measurements made by this method is that of Pividal et al. (1992).

The system of equations we have produced may be used in ways that differ from those illustrated. Equation 16 is very sensitive to the values of x_{S1}, Z_1, and K_i, and can be used as a consistency check on sets of experimental $T - Z_1 - x_{S1}$ data either from the characterization procedure or for measurements on a new system when both γ_1^∞ and γ_2^∞ are measured so that both K_1 and K_2 can be found. Values of R'/S' can be expected to lie in the range $0.5 \leq R'/S' < 1.0$, depending on the relative size of the reboiler. Small errors in K_i, or in the concentrations x_{S1} and Z_1 can easily give physically impossible R'/S' values, for example, $R'/S' > 1.0$ or $R'/S' < 0$.

From our experience with VLE measurement (Raal and Mühlbauer, 1998), for the ebulliometer shown in Figures 1 and 2 we advocate rapid stirring in the reboiler and effective insulation of the upper part with a vacuum jacket. Several authors have added known amounts of solute to their abulliometer(s) by weighing a syringe before and after injection of solute through a sample septum. In a recent development for another purpose, we have produced a micro liquid dispenser of exceptional accuracy operating on a nonsyringe principle (worldwide patents applied for). The instrument is automated, requires no calibration, and can dispense bubble-free liquid in steps of 0.06 μL. (See attached graph of programmed discharge vs. stepper motor revolutions, Figure 6.) This should facilitate the accurate introduction of successive small amounts of solute into an ebulliometer, or sampling of a liquid stream and direct injection into a GC.

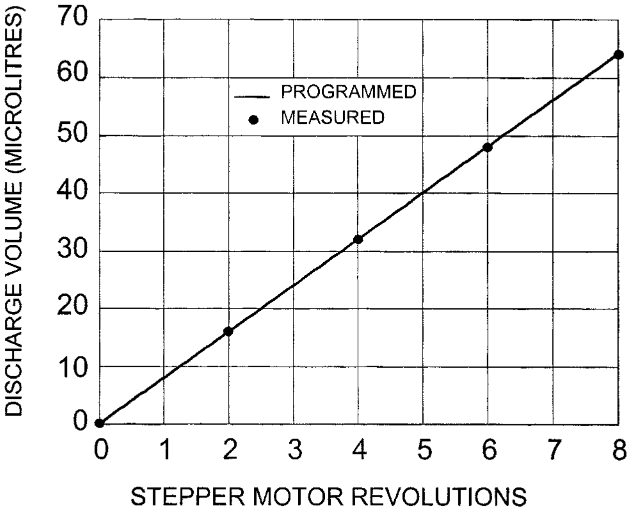

Figure 6. Performance of automated micro liquid dispenser operating on a nonsyringe principle.

It is hoped that improvements in equipment and operating technique, when used together with the system of exact equations presented here, will permit more accurate determination of γ_1^∞ by differential ebulliometry, particularly for systems with large relative volatility.

Acknowledgments

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Notation

A = constant in Porter equation
A_{ij} = constants in Margules equations
D' = dimensionless group defined by Eq. 20a
E = dimensionless ebulliometer constant
F = molar flow rate of fluid in Cottrell pump
f = molar flow-rate ratio V/L
f' = static holdup ratio V'/L'
H_V = equilibrium vapor enthalpy, J/kmol
h_L = equilibrium liquid enthalpy, J/kmol
h_F = enthalpy of stream F (see Figure 3), J/kmol
L = molar flow rate of equilibrium liquid
L' = molar liquid static holdup
P = system total pressure, Pa
p_i^{sat} = pure-component vapor pressure, Pa
R' = molar static holdup in reboiler
S' = molar total charge in ebulliometer
T = equilibrium temperature, K
V = equilibrium vapor molar flow rate
V' = molar vapor static holdup
x_{Si} = mole fraction component i in charge S'
y_i = equilibrium vapor mole fraction
ϕ = molar flow-rate ratio V/L
ϕ' = static holdup ratio V'/L'
$\hat{\phi}_i$ = fugacity of component i in vapor phase, Eq. 9a
ϕ_i^{sat} = saturation vapor-phase fugacity, Eq. 9a.

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Appendix: Derivation of Eq. 16

The equation relating x_{Si}, Z_i, and R'/S' is derived as follows. From Eq. 7:

$$y_i = \frac{S'x_{Si} + L'x_i - R'Z_i}{V'} = \frac{S'x_{Si} - L'y_i/K_i - R'Z_i}{V'}.$$

Solving for y_i give

$$y_i = \frac{x_{Si} - (R'/S')Z_i}{(V'/S') + \dfrac{L'}{S'K_i}}$$

and

$$\sum_{i=1}^{m} y_i = 1 = \sum \frac{x_{Si} - (R'/S')Z_i}{(V'/S') + L'/S'K_i}. \tag{A1}$$

A similar derivation for x_i, by eliminating y_i from $y_i = x_i K_i$, gives

$$\sum_{i=1}^{m} x_i = 1 = \sum \frac{x_{Si} - (R'/S')Z_i}{(L'/S') + V'K_i/S'}. \tag{A2}$$

Term-by-term subtraction of Eqs. 16 and 17 then gives

$$\sum [x_{Si} - (R'/S')Z_i] \times \left\{ \frac{1}{V'/S' + L'/K_i S'} - \frac{1}{(L'/S') + V'K_i/S'} \right\} = 0.$$

We introduce

$$f' = V'/L'. \tag{A3}$$

After some rearrangement, this gives

$$\sum_{i=1}^{m} (x_{Si} - R'/S')Z_i(S'/L') \left\{ \frac{K_i}{1 + K_i f'} - \frac{1}{1 + f'K_i} \right\} = 0$$

$$\sum_{i=1}^{m} (x_{Si} - (R'/S')Z_i)(S'/L') \left\{ \frac{K_i - 1}{1 + K_i f'} \right\} = 0. \tag{A4}$$

Solving Eq. 4a for R'/S', one obtains for a binary mixture (after some tedious algebra)

$$R'/S' = \frac{x_{S1} + D'}{Z_1 + D'} \tag{A5}$$

where

$$D' = \frac{K_2 - 1}{K_1 - K_2} \left\{ \frac{1 + K_1 f'}{1 + f'} \right\}. \tag{A5a}$$

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