Measurement and Application of Limiting Activity Coefficients

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Infinite dilution activity coefficients (γ^∞) in binary liquid mixtures are data of wide practical and theoretical applicability, but their extensive use has been hindered by the experimental limitations of classical vapor-liquid equilibrium techniques. Two new experimental methods for accurate γ^∞ determinations are presented. These techniques, both faster and more accurate than classical methods, are complementary, and their applicability to different types of binary systems is discussed.

SCOPE

The modern design and modeling of fluid-phase separation equipment require an accurate mathematical representation of chemical activities in a multicomponent liquid mixture. Solution models now use binary data only to represent a multicomponent mixture, and have proven central to the rational design of distillation, absorption, extraction, stripping, or even crystallization units. Although many sets of binary data exist in the literature, the limiting factor in most multicomponent process designs is in the acquisition of valid binary data needed to determine parameters in the mathematical models. For most miscible organic systems, the existing data are in the form of classical VLE (vapor-liquid equilibria) measurements, which are intrinsically slow and difficult experiments. Further, the resulting data, even if accurate, do not contain the most useful information either for a basic understanding of solution behavior or for practical application.

It is the purpose of the current study to demonstrate a different approach to gathering the data needed for studying the solution thermodynamics of binary liquid mixtures as well as for designing multicomponent separations. The advantages of using infinite dilution activity coefficients were first proposed over twenty years ago, and their use in design and scale-up has often been demonstrated. However, the actual measurement of such quantities by classical means—either from VLE or LLE data—is very imprecise, and until recently newer experimental methods have been limited in applicability. This work presents two complementary experimental methods for measuring limiting activity coefficients in a wide variety of organic systems. Since these methods are both easier to use and intrinsically more accurate than the classical techniques, the use of limiting activity coefficients presents useful, new experimental and analytical approaches.

CONCLUSIONS AND SIGNIFICANCE

Limiting activity coefficient (γ^∞) data are most effective both in the description of binary mixtures and in the scale-up to multi-component systems. The limiting activity coefficient characterizes the behavior of a single solute molecule completely surrounded by solvent. As such, it generally indicates a maximum nonideality and offers incisive information to the theorist, since the order-disorder effect disappears; it also offers economy of effort to the experimentalist, since this datum has wider applicability than a measurement at any other concentration.

The major reason that γ^∞ methods have been little used lies in the difficulty and limitations of existing experimental techniques. We present new modifications of two experimental methods—ebulliometry and vapor-liquid chromatography (VLC)—which eliminate the most important of these limitations. Classical methods for γ^∞ are unquestionably too imprecise and/or too tedious. We have improved the ease and reliability of older ebulliometric methods, first by limiting our interest to γ^∞ only, and second by the use of a differential technique which minimizes major uncertainties in data analysis. The chromatographic method has been used in the past primarily for very volatile solutes in involatile solvents, but carrier gas presaturation ameliorates that limitation. These two methods, used together, provide a versatility and ease of accurate data-taking previously unavailable. The results of both methods are shown to agree with each other as well as with literature data, where available.

Moreover, the resulting γ^∞ values are shown to be of a precision such that they are at least as useful as the very best VLE data for scaling up to multicomponent systems at far less cost and effort, and they are clearly superior to ordinary classical data. Such a result occurs, because small errors in measured mid-concentration activities are magnified near the end points, whereas even moderate errors in γ^∞ measurements are attenuated in extrapolation to finite concentrations.

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Recent advances in molecular thermodynamics have made possible the accurate generation of multicomponent-multiphase equilibria from binary data only (Abrams and Prausnitz, 1975; Eckert et al, 1965; Prausnitz et al, 1980; Renon et al, 1971; Mertl, 1972). Successful treatments of this type have been reported for a wide variety of multicomponent mixtures, including not only a variety of parafinic, napthenic and aromatic hydrocarbons but also polar and hydrogen binding compounds such as ketones, halides, nitriles, alcohols, and even water. Such methods are now in very common use for the design of separation processes and have proven instrumental in proposing new and improved processes.

Traditionally, the binary data have been vapor-liquid equilibrium (VLE) data or mutual solubilities. Such binary data represent a substantial improvement over the impractical measurement of multicomponent equilibria, but considerable effort must still be expended on classical VLE techniques. Moreover, such techniques become increasingly inaccurate in the dilute regions, which often represent the most important point of separation processes. In addition, adjustable parameters determined from VLE measurements are not unique for many statistical thermodynamic models of liquid mixtures and, therefore, contribute little either to the evaluation of solution models or to the development of parameter correlations.

An attractive alternative to the traditional methods is the direct determination of γ^∞. It has been established that γ^∞ values are sufficient for making very good predictions of multicomponent VLE data; Schreiber and Eckert (1971) have used binary γ^∞ values to predict phase equilibria for five miscible multicomponent systems exhibiting both strong association and solvation. They showed that, for nearly a hundred data points tested in the multicomponent region, the predicted vapor compositions and bubble point temperatures were well within the accuracy of the experimental measurements. This calculation was done with Wilson's equation, but would be equally applicable with any of the newer solutions to the Gibbs-Duhem equation, (Chien and Null, 1972; Hsieh and Eckert, 1974; Abrams and Prausnitz, 1975; Prausnitz et al., 1980).

Up to now, limiting activity coefficients have been determined from extrapolations of classical VLE data. Unless the data are uncommonly accurate and plentiful in the dilute region, their extrapolation to infinite dilution is very imprecise. If a vapor composition method (rather than a total pressure technique) is used, one may calculate activity coefficients from each VLE data point and extrapolate graphically. However, the result statistically overweighs the two or three points at the dilute end, and it is just for these data that the uncertainty in the activity coefficient is the greatest. Recall that neglecting the Poynting correction and vapor phase nonideality, for any component:

$$\gamma_i = \frac{y_i P}{x_i P_i^s} \tag{1}$$

In the dilute region, this expression varies most appreciably with the composition ratio, y_i/x_i, and as one approaches infinite dilution, uncertainties in these very small values make the ratio quite imprecise. Alternatively, one may fit the data to any of the empirical expressions for the excess Gibbs energy, but the γ^∞ value obtained will depend strongly on the mathematical behavior of that particular expression used near infinite dilution (see for example Wong and Eckert, 1971). Such uncertainty is one reason that infinite dilution activity coefficients have been so little used in the past.

Gautreaux and Coates (1955) proposed using γ^∞ 25 years ago, but the data then available were inadequate to demonstrate its utility. However, they were aware of the definite advantages in using limiting activity coefficients, if the experimental values were quickly and reliably available. First, the γ^∞ values represent, in almost all cases, the maximum nonideality in the solution, with solute molecules completely surrounded by solvent. Once these extremes are known, the prediction of lesser nonidealities (in more concentrated solutions) is even more precise. As a result, phase equilibria in concentrated solutions are relatively insensitive to moderate errors in the value of γ^∞ used to calculate them.

In addition, a data base of γ^∞ values would be most useful to any theoretical efforts to predict solution nonidealities from pure component properties only. Infinite dilution lends itself both to group-contribution approaches as well as to statistical thermodynamic interpretation without the problem of communal entropy—the solution to the order-disorder problem becomes trivial. There can be no question of what the nearest neighbors are for a given solute molecule, if it is truly at infinite dilution. In fact, some useful empirical methods have already been developed for predicting γ^∞ values (Derr and Deal, 1969; Null and Palmer, 1969; Fredenslund et al. 1975).

We present here two experimental techniques developed for the rapid and accurate determination of γ^∞ in a wide variety of systems. The methods are not new, but rather represent existing techniques modified to extend their utility to a wider range of systems. A differential ebulliometric method and a chromatographic technique is described below. Each technique is most applicable to systems of different relative volatilities and both capable of evaluating γ^∞ with an accuracy which averages 2% for well-behaved systems, but may rise to ~5% for a few cases where the techniques are only marginally applicable. These two techniques are not only internally consistent, but also agree with each other and with limited literature data which are suitable for comparison.

Differential Ebulliometric Technique

Experimental suggestions for the direct determination of limiting activity coefficients were given by Gautreaux and Coates (1955). They derived four expressions for γ^∞ in terms of pure-component properties and the limiting slopes of pressure and temperature with respect to liquid-and vapor-phase compositions. Though experiments could be designed to measure any of the four slopes, the simplest and most convenient method must include: i) *a priori* gravimetric determination of composition rather than analysis of samples, since several highly dilute compositions are necessary in every run, and ii) dynamic rather than static vapor-liquid equilibrium to assure rapidity of measurement. These constraints result in the determination of the temperature vs. liquid composition limiting slope at constant pressure, i.e., measurements of boiling point elevation. To avoid the errors inherent in measuring absolute rather than differential quantities, a differential ebulliometer is used.

Apparatus

The differential ebulliometer is similar in some respects to that described previously by Null (1970), and by Wong and Eckert (1971). It involves boiling a solution in an ebulliometer connected, through condensers to a common manifold, with a second ebulliometer in which pure solvent only is boiling, Figure 1, thus maintaining the vapor phases of the two boiling liquids at the same pressure. Small fluctuations in pressure have a minimal effect and, in addition, the pressure, and in consequence the temperature, at which γ^∞ is determined, can be readily set and controlled. A vacuum pump is connected through a solenoid valve to the manifold, which includes a 15-L ballast tank. The valve is controlled, through a relay, by a differential sulfuric acid manostat and dry air is continuously bled into the system. Control of better than ±0.03 kPa (±0.2 mm Hg) is achieved in this manner and the pressure is read to better than ±0.01 kPa (±0.1 mm Hg) from a mercury manometer with a cathetometer. The boiling point elevation is measured with a cathetometer. The boiling point elevation is measured with a Hewlett-Packard quartz crystal thermometer (Model 2801A) with matched sensing probes capable of resolution to 0.0001°C. The accuracy of the instrument is certainly less and, in any event, variations in the boiling characteristics of the liquids in the ebulliometers do not permit an accuracy better than 0.001°C in the temperature differences.

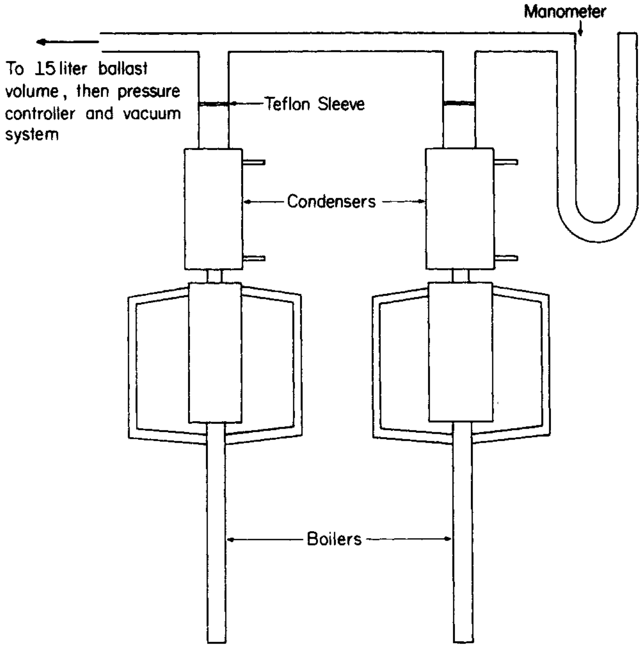


Figure 1. Schematic diagram of ebulliometers connected to vacuum system.

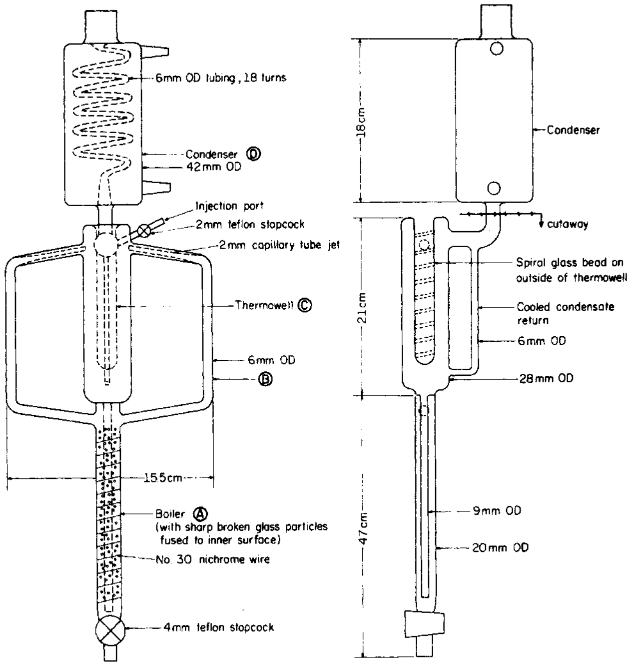


Figure 2. Front and side views of ebulliometer.

The ebulliometer used in this investigation is shown in detail in Figure 2. Like most ebulliometers, it is based on a Cottrell pump; in this case, consisting of two concentric cylinders, separated by a ring seal at the top, between which the liquid is boiling. The outer cylinder is heated by 1.8 m(6 ft) of #30 nichrome wire connected to a variac and has sharp, 24 mesh, particles of ground glass fused to its inner surface for nucleation. Thirty to 50 V are generally applied to the heater. Superheated liquid is pumped up through the side tubes and jets onto the thermometer well, where the superheat is taken up by evaporation. The liquid then passes down the outside of the thermowell, slowed by the helical bead, and returns via the inner cylinder, joined by the cooled condensate. The whole ebulliometer is thoroughly insulated.

To assure that a valid equilibrium temperature is always established on the well, we have investigated the effect of the dimensions of the system, the rate and distribution of heating, and the density of nucleation sites. The measured temperature difference beween the two devices was steady, and independent of moderate changes in the power input to either system. (With carbon tetrachloride as the test solvent, for example, a four-fold increase in power resulted in a temperature rise of only 0.015°C.) Temperature fluctuations never exceeded ±0.001-0.002°C.

The possibility of superheating the liquid diminishes as the surface-to-volume ratio of the boiler is increased. But, using too small a volume of liquid is impractical, since the original liquid composition would be drastically affected by the enrichment of the vapor with the more volatile component. It is in fact this complication that has led to questions about the applicability of ebulliometry to mixtures (Hala, 1967). This design with up to 65 cc of initial solvent volume represents a compromise between the need to leave a substantial liquid volume and the need to avoid excessive superheating. The reference ebulliometer in which only pure solvent is boiling has a smaller volume, about 30 cc.

Procedure

Initially, both ebulliometers are filled gravimetrically with pure solvent to a level about 25 mm(1 in.) from the side tubes. The pressure control is set, the liquid heated to boiling, and the system allowed to come to equilibrium (usually about 30 min.). With both ebulliometers containing pure solvent only, the optimum heating rate and any systematic offset in the measured temperature difference are determined. Either pure solute or a gravimetrically prepared mixture is injected into the mixture ebulliometer through a serum stopper with a syringe (Gastight, #1001) fitted with a luer valve. The syringe weighs about 45 g and is weighed before and after each injection to obtain differences of the order of 1 g, to a precision of ±0.1 mg. When equilibrium is reached again (5-15 min.), the pressure and the temperature difference are recorded. The procedure is usually repeated six times. Approximately an hour after the last point is taken, another boiling point difference is observed. A value different from the last recorded point would indicate a concentration change due to loss of more volatile component through the condenser. This post-measurement boiling point change was always less than 1% the total change for all systems reported. Cycling of the observed temperature difference is generally ~0.002°C and never over 0.005°C. An average value is used and is probably valid to ±0.001. Experimental data for a typical run are shown in Table 1.

TABLE 1. TYPICAL DATA SET: TOLUENE(1)-ETHANOL(2) (P = 176.02 TORR; T = 318.51°K; INITIAL WEIGHT OF SOLVENT: 52.9083 g)

W. of Solute Injected (g)	ΔT(K)	x_1(nominal)	x_1(corrected)
0.4641	−0.118	0.00437	0.00420
0.5399	−0.244	0.00940	0.00905
0.4902	−0.354	0.01392	0.01343
0.5491	−0.472	0.01894	0.01830
0.6278	−0.598	0.02462	0.02383
0.5878	−0.709	0.02988	0.02897

Data Analysis

The ebulliometric data are analyzed following the development of Gautreaux and Coates (1955) with additional terms included to account for the vapor-phase nonideality. A rigorous expression for the activity coefficient at infinite dilution can be

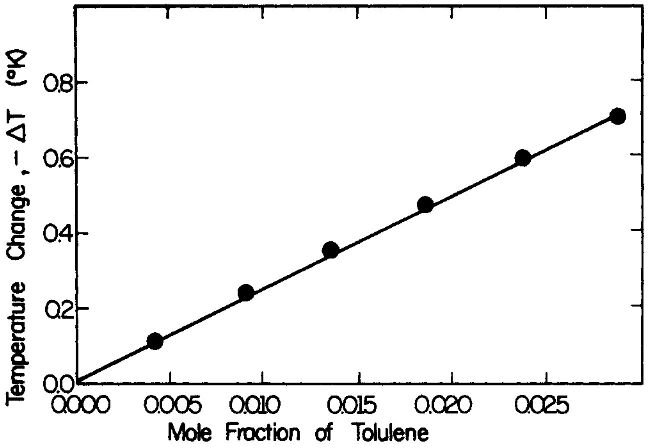


Figure 3. Typical ebulliometric data: temperature changes for toluene in ethanol at 23.41 kPa (176.02 torr).

readily derived in terms of pure component properties and the limiting slope of the temperature vs. composition curve.

$$\gamma_1^\infty = \frac{\phi_1^{(P_2^s)}\left[P_2^s - \Big(1 - \frac{P_s^s v_2}{RT} + \frac{P_2^s}{\phi_2^s}\left(\frac{\partial \phi_2^s}{\partial P}\right)_T\ \right]\left(\frac{dP_2^s}{dT}\right)\left(\frac{\partial T}{\partial x_1}\right)_P^\infty}{P_1^s\phi_1^s\exp[(P_2^s - P_1^s)v_1/RT]} \tag{2}$$

Eq. 2 is based on no assumptions concerning liquid-phase nonideality other than the obvious one of the finiteness of the activity coefficient and of its composition derivative at infinite dilution. The fugacity coefficient terms, not too critical at the atmospheric or lower pressures used here, are obtained from virial coefficients estimated with the method of Hayden and O'Connell (1975). The limiting composition derivative of the temperature, $(\partial T/\partial x_1)_P^\infty$, is obtained directly from the ebulliometric data.

The advantage of using Eq. 2 is that no functional dependence of the activity coefficient on composition is assumed. Instead of extrapolating activity coefficients to their limiting value, an inherently uncertain process, we measure the limiting slopes of nearly linear x-T curves whose end point is always fixed. Values of $(\partial T/\partial x_1)_P^\infty$ are determined by fitting the experimental x-T points to simple algebraic expressions, linear in their coefficients. To ensure the absence of numerical artifice, four different expressions are used and varying numbers of data points are fitted. By considering the standard percent deviation of the fits and the effect of varying the number of data points on the γ^∞ value, the most suitable expression can be found in every case by inspection, and an occasional bad data point spotted.

Often, a two-parameter quadratic expression is found to be adequate as shown in Figure 3, which is the result of Table 1. The enrichment of the vapor above the boiling mixture with the more volatile component plus the holdup of liquid condensate return alter the gravimetrically determined composition of the mixture. This correction (usually a few percent or less) is made by estimating the vapor and liquid condensate volumes (150 and 2 cc respectively, for the design in Figure 2) and solving the appropriate stoichiometric and thermodynamic relationships by iteration.

Eq. 2 can be used to examine the sensitivity of γ^∞ to errors in the measured limiting slope and thus provide a criterion for the applicability of the ebulliometric method to a given binary system. If we disregard the fugacity coefficient terms and the Poynting correction, all of which have minor significance anyway, the equation becomes:

$$\gamma_1^\infty = \frac{P_2^s - \frac{dP_2^s}{dT}\left(\frac{\partial T}{\partial x_1}\right)_P^\infty}{P_1^s} \tag{3}$$

The limiting activity coefficient is essentially the algebraic sum of two terms and may become the difference between too much larger numbers. In this case, extremely high accuracy is needed in the data. We can consider the fractional change in γ^∞ with the equivalent change in the limiting slope as a measure of sensitivity.

$$\frac{\left(\frac{\partial T}{\partial x_1}\right)_P^\infty}{\gamma_1^\infty}\,\frac{d\gamma_1^\infty}{d\left(\frac{\partial T}{\partial x_1}\right)_P^\infty} = 1 - \frac{P^s_2}{P_1^s\gamma_1^\infty} \tag{4}$$

The second term on the right side of the equation is essentially the relative volatility at infinite dilution, since the activity coefficient of the solvent is unity at this limit and the total pressure is the vapor pressure of the solvent. The ebulliometric technique is, thus, seen to be best suited to systems of similar volatility. If the solute, for example, is much less volatile than the solvent, γ^∞ determination will be difficult unless its value is very high. The nonideality would be imposed on the large ideal effect of the vapor pressure difference and, thus, not easily measured in a vapor-liquid equilibrium system of any kind. A case in point is Nitrobenzene in Hexane, a system for which we could obtain no consistent results despite a high degree of nonideality (γ^∞ of about 10 at 308°K), owing to the vast difference in vapor pressures.

If the solute is much more volatile than the solvent, the liquid composition correction becomes critical. While this causes no instability in the data reduction, heavy reliance must be set on the estimated values for the vapor space and the liquid holdup. There is also an increased risk of losing some solute through the condenser during a run. Systems where the solute has a much higher vapor pressure than the solvent are, thus, unsuitable, and so are systems of similar vapor pressures but very high γ^∞ values, a more serious restriction. For such systems, the alternate technique proposed, VLC, gives better results with considerably less effort.

A second method of data reduction was used as an additional test of our technique and an aid in analyzing results for systems where the γ^∞ values are too sensitive to experimental error. The data were simply fitted to empirical expressions for the excess Gibbs energy by minimizing the error in the predicted total pressure, and the limiting activity coefficients were calculated from the adjusted parameters. This process should not be confused with the fitting of classical VLE data with these expressions to obtain parameters and, possibly, limiting activity coefficients. The data here lie exclusively in the dilute region and have been obtained by a technique suited to this region. Extrapolation to infinite dilution can, thus, be made more reliably, although the adjustable parameters obtained may not be applicable to the calculation of activity coefficients over the entire concentration range. The Van Laar, Wilson, and UNIQUAC equations were used, though use of the first two is usually sufficient.

It must be stressed that the limiting slopes technique is preferable to any other, since it is the only rigorous method and should be used alone when internally consistent. For systems well suited to the ebulliometric technique and of moderate nonidealities, results obtained with either method or equation are practically identical. When activity coefficients are high, extrapolation with the empirical equations tend to yield slightly higher values and can be ignored, unless the limiting slope results are too scattered.

Such an analysis of the data of Table 1 is given in Table 2. Although the solute is much less volatile, the boiling point decreases due to the high positive deviations from Raoult's law and the γ^∞ becomes the sum of two positive numbers. The γ^∞ value determined changes little with the liquid composition

TABLE 2. EBULLIOMETRIC DATA FOR SYSTEM TOLUENE(1)-ETHANOL(2) AT 318.51°K

A. Results from Limiting Slope Analysis: $\gamma_1^\infty = 2.352 - 0.1149(dT/dx_1)^\infty$

		Nominal Concentrations Used			Corrected Concentrations Used		
Function	No. of Data Points	Std. % Dev. of Fit	$(dT/dx_1)^\infty$	γ_1^∞	Std. % Dev. of Fit	$(dT/dx_1)^\infty$	γ_1^∞
$\Delta T = ax_1 + bx_1^2$	5	0.833	−27.23	5.48	0.856	−28.35	5.61
	6	0.836	−27.13	5.47	0.873	−28.24	5.60
	7	0.855	−27.04	5.46	0.906	−28.13	5.58
$\Delta T = ax_1 + b\ln(1 + x_1)$	5	0.893	−27.25	5.48	0.856	−28.39	5.61
	6	0.872	−27.16	5.47	0.860	−28.28	5.60
	7	0.868	−27.08	5.46	0.882	−28.18	5.59
$\Delta T = ax_1 + bx_1^2 + cx_1^3$	5	0.263	−27.97	5.56	0.266	−29.15	5.70
	6	0.536	−27.54	5.52	0.543	−28.70	5.65
	7	0.565	−27.42	5.50	0.572	−28.57	5.63

B. Results from Total Pressure Fits (All Data Used)

	Nominal Concentrations Used		Corrected Concentrations Used	
Equation	Std. % Dev. of Fit	γ_1^∞	Std. % Dev. of Fit	γ_1^∞
Van Laar	0.009	5.52	0.006	5.62
Wilson	0.054	5.72	0.035	5.78
UNIQUAC	0.050	5.71	0.028	5.75
	$\gamma_1^\infty = 5.60$			

correction and the method of analysis. The logarithmic expression, which is very similar to the quadratic one, gives the most consistent results and 5.60 can be considered the best value. This happens to agree well with the value of 5.62 obtained with the Van Laar equation. Thus, there is no reason here to consider the Wilson equation result of 5.78, or that of the UNIQUAC, 5.71. Additional details of the experiment are available elsewhere (Newman, 1977; Nicolaides, 1977).

Gas Chromatographic Method

A gas chromatograph represents merely a multistage separation process and can be used to measure accurate vapor-liquid equilibria at infinite dilution using very small quantities of material. Such a technique was first proposed by Martin (1956) and has been widely used to determine γ^∞ for very volatile solutes in very involatile (high-boiling) solvents. In recent years, there have been some applications of the technique to systems containing more volatile solvents (Pecsar and Martin, 1966; Barker and Hilmi, 1967; Yodovich, et al., 1971; Leroi et al., 1977). We have adapted and modified such techniques and have utilized a system such as that in Figure 4 to measure activity coefficients in systems, where the solvent is less volatile or only slightly more volatile than the solute.

This application of the chromatographic technique to volatile solvent systems is achieved by taking a helium carrier gas and saturating this gas with the solvent being used. The carrier gas is passed through both a presaturator outside the temperature bath and a second presaturator chromatograph column inside the temperature bath. The presaturated carrier gas stream is then split, half of it running through the heated sample injector block and then through the well-thermostatted test column, in which the solvent is the stationary phase. The half running through this column then runs through one side of the detector, while the other half from the presaturated feed runs through the other side. The detector used is a thermal conductivity detector, as the large amounts of solvent present would saturate a flame ionization detector.

The limiting activity coefficients are found directly from the residence time on the column of very small amounts of solute material injected into the test side of the carrier gas flow. When suitable precautions are taken, γ^∞ for the solute is expressed in terms of the solvent moles in the column, M_1, and the retention time, given effectively as the volume difference between the total carrier flow through the column during retention, V_u^0, and the void volume of the column V_m:

$$\gamma_2^\infty = \frac{M_1 RT\, \phi_2 z_{mix}}{\phi_2^s P_2^s (V_u^0 - V_m)} \tag{5}$$

where the gas-phase nonideality is accounted for in the same manner as above: by a truncated virial equation. Since the total pressure rarely exceeds 113 kPa (850 torr), this procedure is certainly adequate.

Flow rates were controlled by a Hoke precision flow controller and measured on the exit side by a bubble flowmeter at the outlet accurate to better than ±0.5%. Pressure drop across the column was measured with a mercury manometer. Solvent loadings were determined by two different procedures, which checked against each other to better than 1% on all runs for which both were used. The first involved weighing the column after a run, washing out the solvent with acetone, drying and reweighing. The second method used Eq. 4 with a previously-known value of γ^∞ for a test solute, used to back-calculate the loading. The second method proved especially convenient for lower solvent loadings where slight stripping could occur.

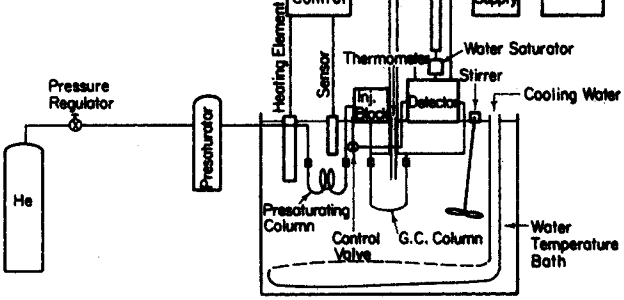


Figure 4. Schematic diagram of modified gas chromatographic technique for measuring limiting activity coefficients in volatile solvents.

TABLE 3. TYPICAL DATA BY VLC METHOD: LIMITING ACTIVITY COEFFICIENTS IN BENZENE AT 20°C

Solute	Run 25[a]	Run 69[b]	Run 70[c]	Literature
Carbon Tetrachloride	1.13			1.13[d] 1.13[e] 1.14[f] 1.14[g]
Carbon Disulfide	1.48	1.51	1.48	
Methylene Chloride		0.90	0.92	
Methyl Iodide	1.18	1.17	1.18	
Ethyl Bromide		1.01 1.01	1.01	
Ethyl Iodide	1.14	1.12		
n-Propyl Chloride	1.06	1.06	1.03	
Acetone	1.77	1.72 1.73	1.71	1.74[h]
Acetonitrile	3.21	3.47	3.39	
t-Butyl Chloride	1.29	1.28	1.28	
Isoprene		1.24	1.26	
Cyclohexane	1.74	1.74		1.74[h]
n-Hexane	2.21	2.21 2.22	2.28	

[a] Fluoropak 80 packing, 6% solvent loading.
[b] Chrom. W packing, 15% solvent loading.
[c] Chrom. W packing, 12% solvent loading.
[d] Barker and Hilmi, 1967.
[e] Ellis and Jonah, 1962.
[f] Scatchard et al., 1940.
[g] Fowler and Lim, 1956.
[h] Extrapolated from ebulliometric data taken over a range of temperatures (Nicolaides, 1977).

It was necessary to keep the column fairly short, 20-30 cm, to minimize both the pressure drop and the axial dispersion of a solute peak. Any pressure drop resulted in some bleed of a volatile solvent from the column. But, as long as the pressure differential was kept around 1-3 kPa (1-2 cm of Hg), this loss was minimal and could be accounted for by periodic runs of standard solutes. This technique is similar to that of Barker and Hilmi (1967).

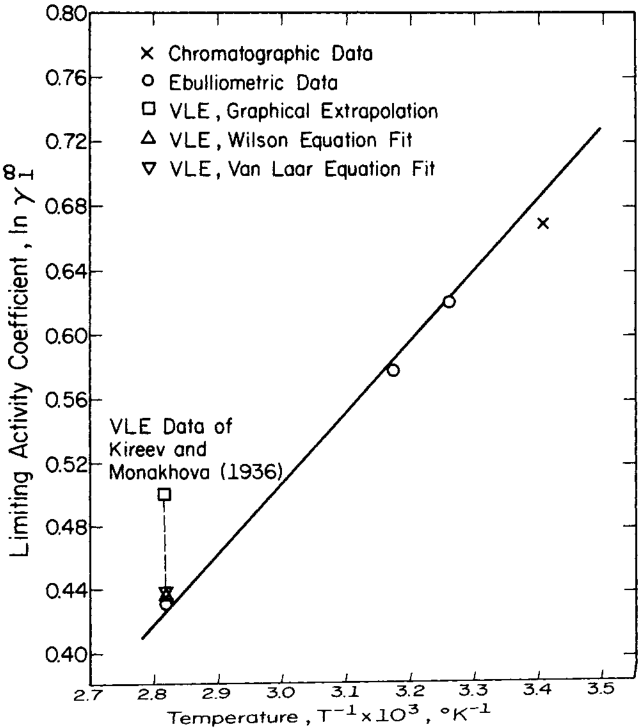


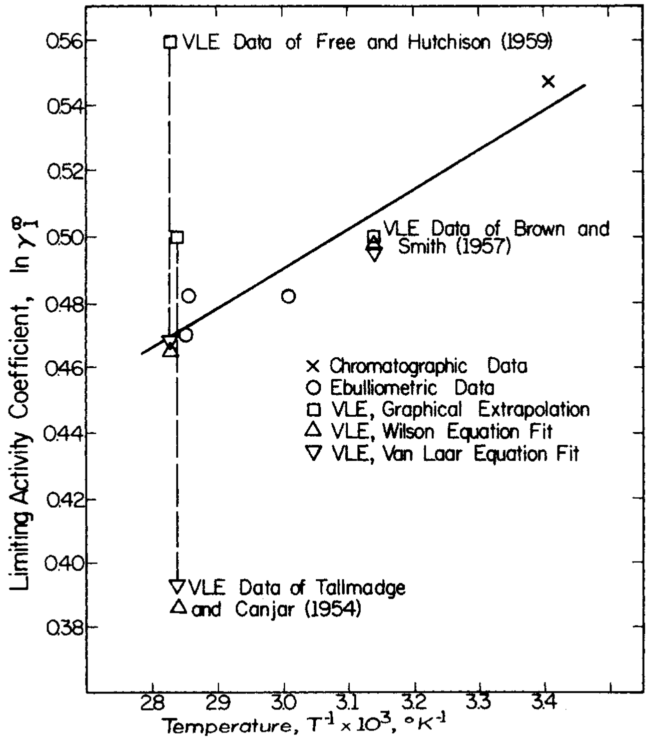
Figure 5. Effect of temperature on the activity coefficient of carbon tetrachloride infinitely dilute in 1,2-dichloroethane.

One additional possible problem is imperfect establishment of equilibrium in the column. This can be caused either by too large a ratio of solute/solvent or by interfacial effects. Our studies used two different substrates (packings) in the columns; an acid washed diatomaceous earth, chromosorb W AW-DMCS and an inert Teflon Fluoropak 80. Both were about a 45/60 mesh in 6-mm (1/4″) copper tubing, and the coating technique of Parcher and Urone (1964) was used. The Chromosorb is a polar material, requiring loadings in excess of about 14% to avoid surface effects, whereas the nonpolar teflon could be used with solvent loadings as low as 1.5%. Solute injections were kept at 0.005 μL for the Chromosorb packing, but could go as high as 1 μL on the Fluoropak. Both solvent loadings and injection sizes were varied over a wide range to assure operation at equilibrium and at infinite dilution.

This technique has a number of distinct advantages. Although solvents must be quite pure and good temperature and flow control are essential, solute purity is not critical and this technique has even been used for reacting solutes (as long as reaction is incomplete, a retention time may be determined). Even with replication, it is quite possible to measure several dozen points per day, which compares most favorably with the very long equilibration times required for classical VLE measurements. Moreover, most of the components used in the apparatus are commercially available.

The greatest drawback of this technique is the lower limit on the volatility of the solute—if it does not pass through the column or passes so slowly that axial diffusion (peak spreading) is significant, the results are not useful. Similarly, there is an upper temperature limit for each solvent material, above which stripping would become unacceptable. In principle, one could operate above the boiling point of the solvent by maintaining an elevated pressure inside the whole apparatus. But, we have not yet attempted to do so.

As an example, a typical data set is presented in Table 3. Both replicate runs and agreement with literature data are within 2%,



ACTIVITY COEFFICIENTS OF ACETONE INFINITELY DILUTE IN BENZENE

Figure 6. Effect of temperature on the activity coefficient of acetone infinitely dilute in benzene.

and data are shown for three experimental runs at different solvent loadings on two different substrates. More extensive data including detailed description of the procedure and apparatus are available elsewhere (Newman, 1977; Long, 1977).

Results and Discussion

To verify the applicability of these techniques for measuring infinite dilution activity coefficients, the results of both ebulliometric and gas chromatographic measurements, over a range of temperatures, were compared with existing experimental data taken by classical VLE techniques. The results of such comparisons are shown in Figures 5, 6, 7 and 8 for four different systems. To appreciate these figures, one must recognize that the quantity being plotted on the ordinate is a vastly expanded scale of ln γ^∞ and that three points are shown for each literature determination of VLE results. These three points represent three different methods of extrapolating to infinite dilution and may be considered to constitute a measure of the uncertainty in the limiting activity coefficient as evaluated from literature VLE data. This does not in any way constitute a deprecation of the literature VLE data, but rather shows only the difficulty in extracting γ^∞ from such measurements.

The three methods used to get γ^∞ from the classical VLE data were a total pressure fit using the Van Laar equation, a total pressure fit using the Wilson equation, and a graphical extrapolation of the points in the dilute region. As can be seen from the plots, these three methods frequently give very different results for the infinite dilution activity coefficients, varying by 10-20% or even more. Our results from both the gas chromatographic method and the ebulliometric method are roughly colinear and a best line through them shows a scatter of under 2%. In all cases investigated, the line falls within the uncertainty range of the literature data. It is unfortunate that more accurate measurements of γ^∞ from classical VLE data are not available for comparison, but it is for precisely that reason that we have developed these two methods. Their precision and their consistency with each other give us confidence that this is an extremely promising approach. That is, these new techniques are both more precise and more rapid than the older VLE methods to get γ^∞, and they contribute to an improved approach to the gathering of thermodynamic data and the rational design of separation equipment.

Partial Molal Excess Enthalpy

The plot of ln γ^∞ linear in reciprocal temperature stems directly from regular solution theory, but also implies a constant value of the partial molal enthalpy at infinite dilution.

$$R\left(\frac{\partial \ln \gamma^\infty}{\partial\, 1/T}\right)_P = \bar{h}_i^{E\infty} \qquad (6)$$

The same quantity can also be determined from the limiting slope of heat of mixing calorimetric data. Clearly, both the ebulliometric technique developed here and most calorimetric methods in existence are not, nor are they intended to be, accurate enough for a $\bar{h}_i^{E\infty}$ determination but a rough agreement may be expected. The heat of mixing data of Stokes et al. (1969) for the Benzene(1)-Cyclohexane(2) system at 25°C are probably the best calorimetric data available for any system. By fitting six of their data points, all in the dilute region, at either end of the concentration range to a quadratic expression, we have obtained at 25°C,

$$\bar{h}_1^{E\infty}/R = 375\ (^\circ\mathrm{K}) \text{ and } \bar{h}_2^{E\infty}/R = 420\ (^\circ\mathrm{K}).$$

By fitting γ^∞ values measured with the methods described to

$$\ln \gamma_i^\infty = \text{const} + \bar{h}_i^{E\infty}/T \qquad (7)$$

we obtain

$$\bar{h}_1^{E\infty}/R = 369\ (^\circ\mathrm{K}) \text{ and } \bar{h}_2^{E\infty}/R = 303\ (^\circ\mathrm{K}).$$

The close agreement in the $\bar{h}_1^{E\infty}$ values is largely fortuitous and cannot be expected in general. The 25% or so agreement in the $\bar{h}_2^{E\infty}$ values is quite good considering the demands made on both

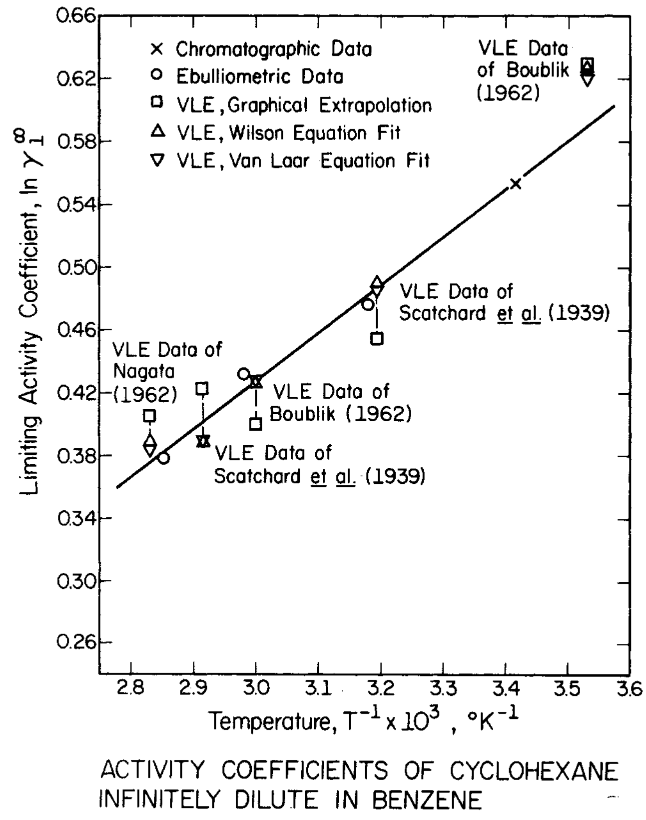


Figure 7. Effect of temperature on the activity coefficient of cyclohexane infinitely dilute in benzene.

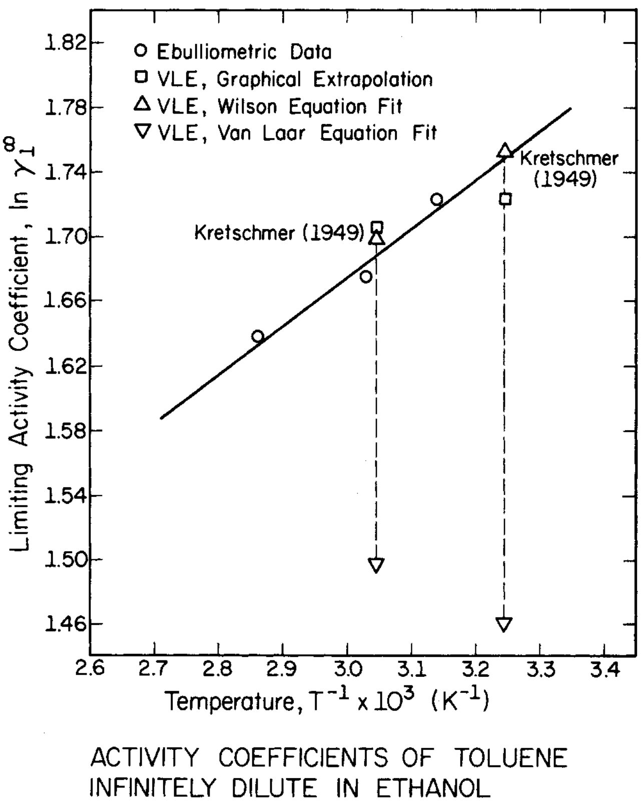


Figure 8. Effect of temperature on the activity coefficient of toluene infinitely dilute in ethanol.

kinds of data by this comparison which, in addition, presupposes that $\overline{h}_i^{E\infty}$ is not a function of temperature. For the Toluene(1)-Ethanol(2) system, the data of Van Ness (1967) were used and similar results were obtained. From the calorimetric data,

$$\overline{h}_1^{E\infty}/R = 326\ (^\circ\mathrm{K})\ \text{at}\ 318.15^\circ\mathrm{K},$$

and

$$\overline{h}^{E\infty}/R = 431\ (^\circ\mathrm{K})\ \text{at}\ 333.15^\circ\mathrm{K}$$

while the ebulliometric results give,

$$\overline{h}^{E\infty}/R = 301\ (^\circ\mathrm{K}).$$

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NOTATION

M_1 = number of solvent moles in chromatographic column
P = total pressure
P_i^s = vapor pressure of component i
R = gas constant
T = absolute temperature
v_i = liquid molar volume of component i
V_u^o = volume of carrier gas flown through chromatographic column
V_m = void volume of chromatographic column
x_i = liquid mole fraction of component i
y_i = vapor mole fraction of component i
z_{mix} = compressibility factor

Greek Letters

γ_i = activity coefficient of component i
γ_i^∞ = activity coefficient of component i at infinite dilution
ϕ_i^P = fugacity coefficient of component i at total pressure P
ϕ_i^s = fugacity coefficient of pure component i at its saturation pressure

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