A MODIFIED EBULLIOMETER FOR MEASUREMENT OF INFINITE DILUTION ACTIVITY COEFFICIENTS

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PREFACE

An existing design of an ebulliometer was modified by the addition of a vane-type magnetic pump to improve the performance of the ebulliometer at low pressures. The modified apparatus was used to determine the activity coefficients at infinite dilution of seven binary systems at three operating pressures each by the technique known as differential ebulliometry. The experimental results can be used to determine predictive model parameters which are of significant interest because of their ease of use and general applicability in phase equilibrium calculations.

I wish to express my very sincere appreciation to my advisor, Dr. Robert L. Robinson, Jr., for his constant support throughtout the course of this study. I thank Mr. M. Wayne Adkins for his contribution to this work through the construction of all glassware including the modified ebulliometer. I thank Mr. Heinz Hall for his contribution in fabricating the magnetic vane-type pump. I would also like to thank Mrs. Kelly Whitfield for her contribution in typing the entire thesis.

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LIST OF SYMBOLS

Symbol	
A	Rackett Equation Constant
A_1, A_2, A_3	Antoine Equation Constants
K_i	equilibrium ratio, y/x, for component "i"
m	mass
MW	molecular weight
n	number of moles
P	pressure
P_i^s	vapor pressure of component "i"
P_c	critical pressure
R	universal gas constant
T	temperature
T_c	critical temperature
V	volume
v	specific volume
x	liquid mole fraction
y	vapor mole fraction
z	overall mole fraction

Greek symbols	
γ^∞	infinite dilution activity coefficient
ϕ	fugacity coefficient
μ	chemical potential

Λ	Wilson Equation parameter
λ	Wilson Equation parameter

Subscripts

1	solute
2	solvent
C	critical property
i	component number
x	liquid property
y	vapor property
z	liquid property during experimental run

Superscripts

∞	infinite dilution property
L	liquid phase property
V	vapor phase property
s	saturated
p	reference pressure

CHAPTER I

INTRODUCTION

The behavior of a compound in a mixture is different from its behavior in the pure state. This difference in behavior is due to the interactions among the unlike molecules which comprise the mixture. If there were no differences in the interactions among different molecules, the properties of a compound would be the same in both the pure state and the mixture, and the mixture would be "ideal". However, in reality there are differences in interactions among different molecules. The activity coefficient is a measure of the extent of non-ideality in the behavior of a liquid in a solution. When the activity coefficient is determined at infinite dilution (i.e., one component is present in very small quantity) in a binary system, the only kind of interaction that exists for a dilute molecule is with the solvent molecules surrounding it.

Infinite dilution activity coefficients can be determined in several ways, one of which is differential ebulliometry. Recently, ebulliometers have been used extensively to obtain infinite dilution activity coefficients (4, 13, 30). However, problems have been encountered in the operation of these devices at low pressures (30). The primary objective of this work was to develop and test a new ebulliometer for improved operation at low pressures. Operation at pressures below atmospheric will enable one to study heavy compounds.

These heavy compounds have very high boiling point temperatures at atmospheric pressure and are unsuitable for the ebulliometric technique.

The plan of attack in the present work was to perform an initial study of mixtures of light hydrocarbons, representing normal paraffins, naphthenes and aromatics. If these results were satisfactory, heavier solute-solvent pairs would be studied in future work.

Ebulliometry is the measurement of the boiling point temperature of a liquid. Differential ebulliometry is the measurement of the change (elevation or depression) in the boiling point of a pure substance as a result of the addition of a small amount of solute.

A knowledge of the rate of change of the boiling point temperature with solute composition enables one to calculate the infinite dilution activity coefficient. These infinite dilution activity coefficients fix the end points of the activity coefficient-composition relationship.

Once infinite dilution activity coefficients have been determined experimentally, they can be compared to values obtained using models for activity coefficient behavior. For example, equations of state could be "tuned" using interaction parameters (k_{ij}) in order to predict mixture properties more accurately. One such equation of state is Soave's modification of the Redlich-Kwong Equation of State:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \tag{1}$$

where

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{2}$$

$$a_{ij} = (1-k_{ij})\, a_i^{1/2} a_j^{1/2} \tag{3}$$

$$a_i(T) = a_{ci}\alpha_i(T) \tag{3.a}$$

$$a_{ci} = 0.42747 \frac{R^2 T_{ci}^{\;2}}{P_{ci}} \tag{3.b}$$

$$\alpha_i(T) = [1 + m_i(1 - T_{Ri}^{\;0.5})]^2 \tag{3.c}$$

$$m_i = 0.480 + 1.574\omega_i - 0.176\omega_i^{\;2} \tag{3.d}$$

$$b = \sum_i x_i\, b_i \tag{4}$$

$$b_i = 0.08664 \frac{RT_{ci}}{P_{ci}} \tag{4.a}$$

The fugacity and activity coefficient are then calculated using the following general thermodynamic relationship:

$$RT\,\ln\left(\frac{f_i}{Py_i}\right) = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{V,T,n_j} - \frac{RT}{V}\right]dV - RT\ln Z \tag{5}$$

$$\ln\left(\frac{f}{P}\right) = \int_0^P \left(\frac{v}{RT} - \frac{1}{P}\right)dP \tag{5.a}$$

$$\gamma_i = \frac{f_i}{x_i f_i^{0}} \tag{6}$$

f_i = fugacity of component i

$f_i^{\,0}$ = standard state fugacity of i.

In Equation (6), f_i is calculated using Equation (5) and f_i^0 is calculated using Equation (5.a), where $f = f_i^0$, i.e., the standard state fugacity is defined as the condition where only pure liquid i is present ($x_i = 1$). x_i in Equation (6) is the liquid mole fraction of component i.

Infinite dilution activity coefficients can be used to predict vapor-liquid equilibrium constants which are of great importance in the separation and mass transfer industrial processes. They are also of interest to statistical thermodynamicists by allowing them to neglect the order-disorder problems which are caused by the solute-solute interactions which are absent in the infinitely dilute region (30).

The greatest importance of infinite dilution activity coefficients is that they can be used to optimize activity coefficient models such as the Wilson Equation, given below.

$$\ln \gamma_k = - \ln[\sum_{j=1}^{c} (x_j \Lambda_{kj})] - \sum_{i=1}^{c} [\frac{x_i \Lambda_{ik}}{\sum_{j=1}^{c} (x_j \Lambda_{ij})}] \qquad (7)$$

which for a binary system can be written as:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}] \qquad (8.a)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}] \qquad (8.b)$$

x_i = liquid mole fraction of component "i"

γ_k = activity coefficient of component "k"

Λ_{ij} = binary interaction parameters

When insufficient data are available to determine binary Wilson parameters from a best fit of activity coefficients over the entire range of composition, infinite dilution activity coefficients can be used. At infinite dilution, Equations (8.a) and (8.b) reduce to:

$$\ln \gamma_1^\infty = 1 - \ln \Lambda_{12} - \Lambda_{21} \quad (x_1 = 0, \; x_2 = 1) \qquad (9.a)$$

$$\ln \gamma_2^\infty = 1 - \ln \Lambda_{21} - \Lambda_{12} \quad (x_1 = 1, \; x_2 = 0) \qquad (9.b)$$

If infinite dilution activity coefficients are known, Equations (9.a) and (9.b) can be solved simultaneously to obtain the binary interaction parameters Λ_{12} and Λ_{21}.

If temperatures corresponding to γ_1^∞ and γ_2^∞ are not equal, Λ_{ij} (which are used only under isothermal conditions) are corrected for the effect of temperature and new parameters $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{12} - \lambda_{22})$ are obtained as follows:

$$(\lambda_{12} - \lambda_{11}) = -RT \ln(\frac{v_1^L}{v_2^L} \Lambda_{12}) \qquad (10.a)$$

$$(\lambda_{12} - \lambda_{22}) = -RT \ln(\frac{v_2^L}{v_1^L} \Lambda_{21}) \qquad (10.b)$$

In the present study, since the data obtained were isobaric and not isothermal, Equations (10.a) and (10.b) would be used to obtain the binary interaction parameters $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{12} - \lambda_{22})$, which are generally regarded as being temperature independent.

CHAPTER II

LITERATURE REVIEW

1. Previous Apparatus

Ebulliometers are used for very accurate measurements of the boiling points of liquids. In 1925, Swietoslawski (28) used the Cotrell pump principle to design a very accurate ebulliometer. The Cotrell pump is a small diameter (about 5 mm) glass tube connected to the boiler of an ebulliometer through which the boiling liquid and vapor mixture passes as a result of thermosiphon action. Ebulliometers have been used for determining the boiling point, the molecular weight, mutual solubilities, sample purities, and infinite dilution activity coefficients.

Eckert et al. (30) at the University of Illinois designed a new ebulliometer by modifying the Swietoslawski model. The advantage of the new design was that it prevented the volatile components from escaping from the system and it also reduced pressure fluctuations. This was accomplished by connecting the modified Swietoslawski ebulliometers (through their condensers) to a common manifold.

The design of the present work is a modification of Thomas' (one of Eckert's coworkers) design (30). Thomas' design is shown in Figure 1. As can be seen in the figure, there are six sections in the ebulliometer.

Section D is the boiler where the solution boils in the annulus between the inner and outer tubes. Crushed glass is fused to the inside

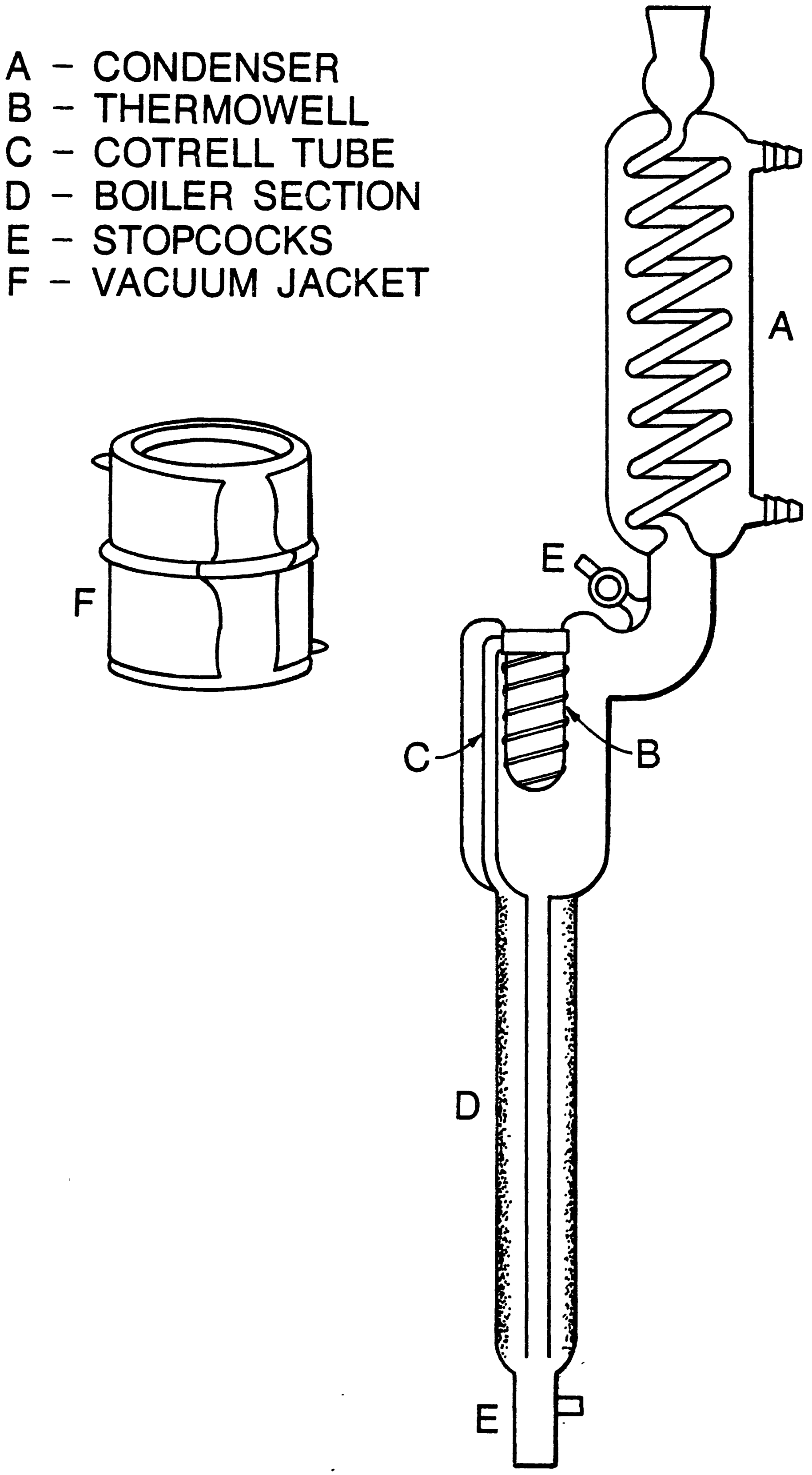


Figure 1. Ebulliometer of Eckert

of the outer tube to provide nucleation sites where the boiling can take place. A stopcock at the bottom of the boiler allows for drainage.

Section C is the Cotrell pump through which the boiling liquid and vapor travel by the boiling action and are delivered to the glass spiral on the thermometer well.

Section B is the thermometer well which is filled with mineral oil and houses the thermometer probe. The glass spiral on the outside of the thermometer well causes the liquid to be distributed evenly on the wall of the thermometer well. This provides enough contact area for the evaporating liquid to reach equilibrium with its vapor. The equilibrium temperature is the temperature registered by the thermometer probe inside the well.

Section A is the condenser where the vapor is totally condensed. There is a Teflon stopcock at the bottom of the condenser where solute is injected and carried to the bulk of the solution by the condensing vapor. This stopcock is also used for (gravimetric) filling of the ebulliometer.

Sections C and B of the ebulliometer are enclosed in a glass vacuum jacket F, which insulates the thermometer well from the surroundings. Section E consists of the stopcocks used for loading and drainage.

Heating is accomplished by a 5 ft long (15-20 Ω) nichrome wire wrapped around the boiler in a helix and connected to a powerstat. The cooling in the condenser is provided by a water-ethylene glycol solution in a refrigerated circulating bath.

2. Theory

Gautreaux and Coates (9) derived the mathematical expression for the experimental determination of the infinite dilution activity coefficient. The derivation by Null (16) is reproduced in Appendix B.

$$\gamma_1^{\infty} = \frac{\phi_1^{(P_2^S)} \{P_2^S - [1 - \frac{P_2^S V_2}{RT} + \frac{P_2^S}{\phi_2^S} (\frac{\partial \phi_2}{\partial P})][\frac{dP_2^S}{dT}][\frac{dT}{dx_1}]_P^{\infty} \}}{P_1^S \phi_1^S \exp[(P_2^S - P_1^S)\dot{V}_1/RT]} \qquad (11)$$

where "1" refers to the infinitely dilute solute component and "2" refers to the solvent.

Neglecting the fugacity coefficient and Poynting correction effects, which are very close to unity at low pressures (in most cases), the above expression reduces to:

$$\gamma_1^{\infty} = \frac{P_2^S - (\frac{dP_2^S}{dT})(\frac{dT}{dx_1})_P^{\infty}}{P_1^S} \qquad (12)$$

The saturated vapor pressures P_1^S and P_2^S and the derivative of the saturated vapor pressure of the solvent with respect to temperature are all pure component properties and can be determined experimentally and represented by an empirical equation such as the Antoine Equation.

The derivative of the boiling point temperature with respect to solute composition at constant total pressure and at infinite dilution is the only term in the above expression which requires binary data. This is the quantity which is determined experimentally using differential ebulliometry.

In practice, small incremental amounts of solute are added to the solvent, and the change in the boiling point temperature is measured. The slope of these data at $x_1 = 0$ represents the $(\frac{dT}{dx_1})_P^\infty$ term, which permits calculation of γ_1^∞ from Equation (12).

Equation (12) can be used to examine the sensitivity of γ_1^∞ to errors in the measured limiting slope and thus provide a criterion for the applicability of the ebulliometric method to a given binary system (6). The limiting activity coefficient is essentially the algebraic sum of two terms and may become the difference between two much larger numbers. In this case, extremely high accuracy is needed in the data. The fractional change in γ_1^∞ with the equivalent change in limiting slope can be considered as a measure of sensitivity:

$$\frac{(\frac{\partial T}{\partial x_1})_P^\infty}{\gamma_1^\infty} \frac{d\gamma_1^\infty}{d(\frac{\partial T}{\partial x_1})_P^\infty} = 1 - \frac{P_2^s}{P_1^s \gamma_1^\infty} \qquad (12.a)$$

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. According to Equation (12.a), systems where the solute has a much higher vapor pressure than the solvent ($P_2^s \ll P_1^s$), and systems of similar vapor pressures ($P_1^s \sim P_2^s$) but very high γ_1^∞ values are unsuitable for the ebulliometric method. The ebulliometric technique is, thus, seen to be best suited to systems of similar volatility (6).

CHAPTER III

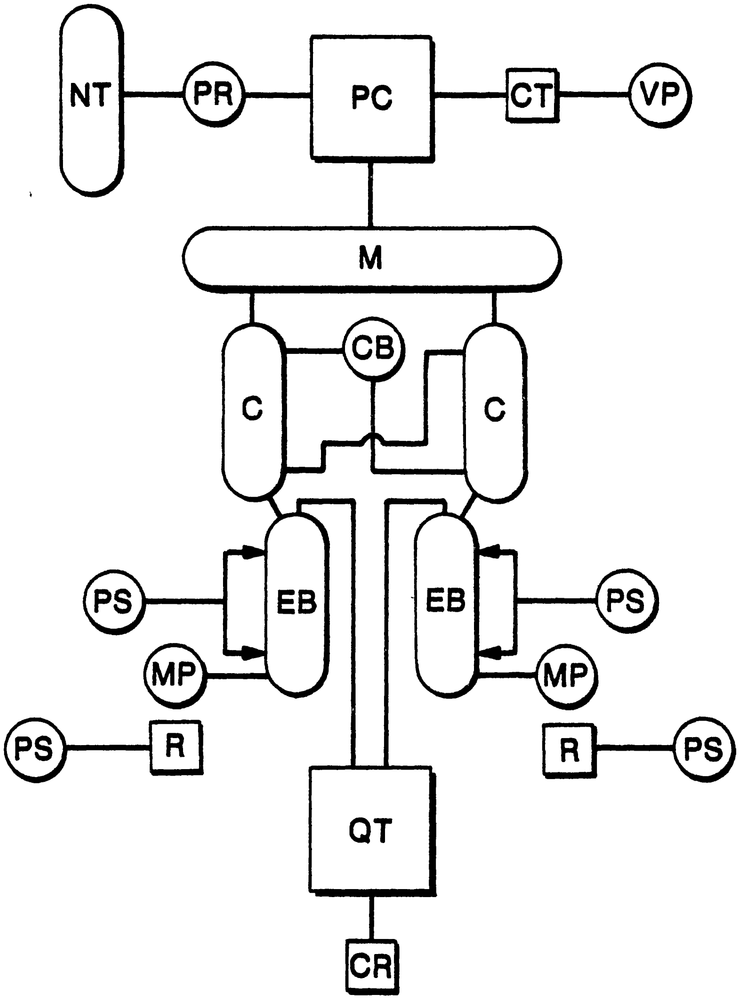
EXPERIMENTAL APPARATUS

In order to achieve better operation at low pressures, the ebulliometer of Eckert et al. was modified in this work. The equipment used in the present work for the experimental determination of infinite dilution activity coefficients is shown schematically in Figure 2. The major components are described below.

The Ebulliometer

The glass ebulliometer shown in Figure 3 is the central component of the apparatus. The design used in the present work is different from the Thomas design, discussed in the previous section and illustrated in Figure 1, in three areas. First, the Teflon stopcock was replaced by a Teflon septum and its position altered from the bottom of the condenser to the top of the thermometer well encasement, thus ensuring the mixing of the solute and the solvent even at low condensation rates. The condenser in this design is also different in that it has two spherical enlargements in the lower section where 80 to 90 precent of the condensation takes place. (The condensation ring could usually be seen at the top of the lower section during the course of most exprimental runs.)

Second, in this design two Cotrell tubes were used in order to distribute the boiling liquid more evenly across the glass spiral on the thermometer well.



NT – NITROGEN TANK
PR – PRESSURE REGULATOR
PC – PRESSURE CONTROLLER
CT – COLD TRAP
VP – VACUUM PUMP
M – MANIFOLD
CB – COOLANT BATH
C – CONDENSER
EB – EBULLIOMETER
PS – POWERSTAT
MP – MAGNETIC PUMP
R – DRIVE MAGNET ASSEMBLY
QT – QUARTZ THERMOMETER
CR – CHART RECORDER

Figure 2. Overall Schematic View of the Apparatus

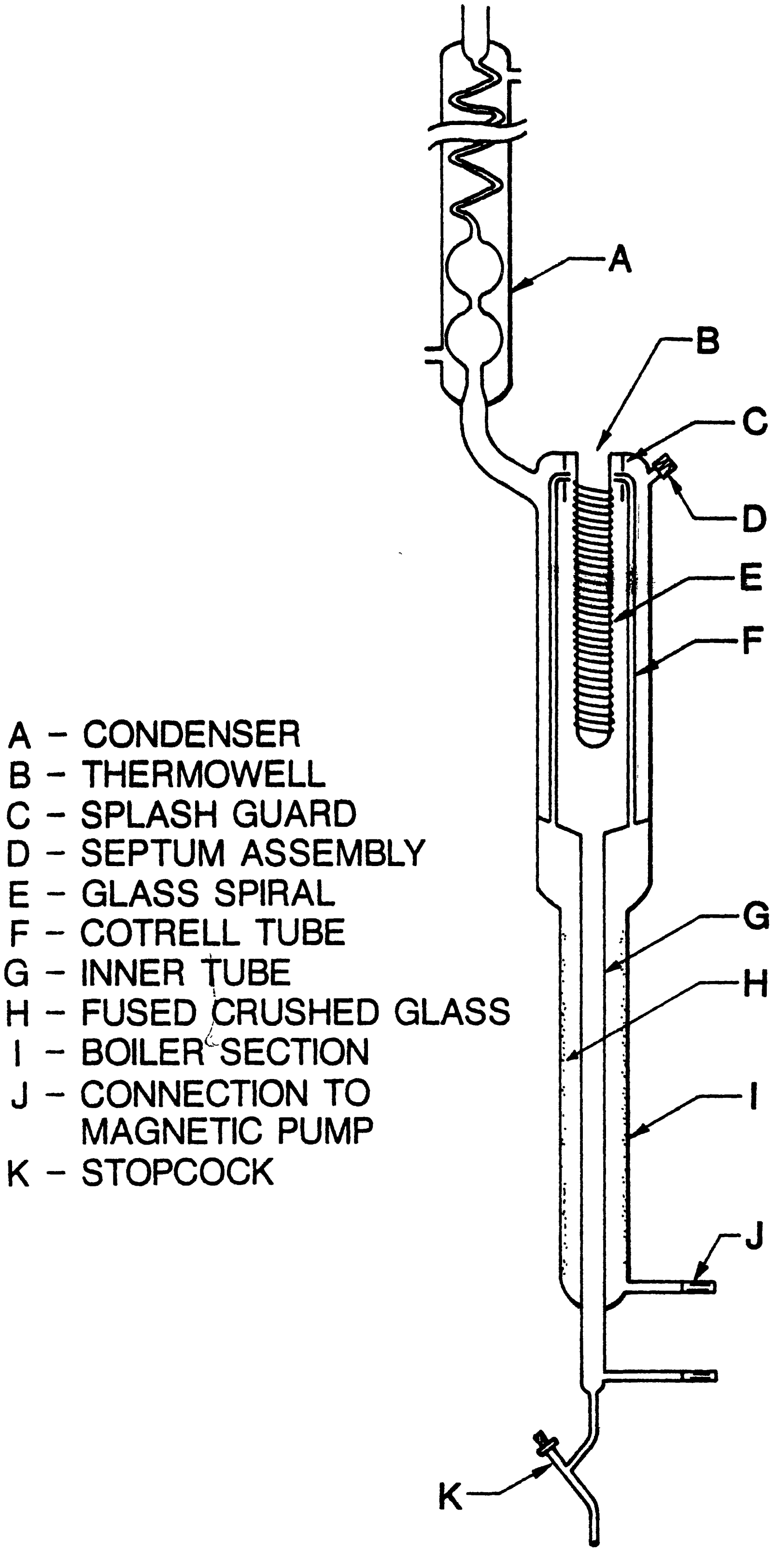


Figure 3. Modified Ebulliometer

The third change, which is also the most important modification, is the addition of a vane-type magnetic pump. This modification was designed to reduce reported problems (30) in operation at low pressures, where boiling becomes unstable (surge boiling) and boiling temperatures fluctuate. The present design replaces the thermosiphon-dependent circulation inside the Cotrell tubes by forced circulation. This leads to better performance of the ebulliometer by constantly covering the thermometer well with a uniform layer of boiling liquid. The new feature enhanced the performance of the ebullimeter, specially at low pressures, as will be discussed in later sections. The result is a decrease in temperature fluctuations caused by the unsteady boiling.

An additional minor change was the deletion of the vacuum jacket. This decision was made because the surrounding room temperature should not have any effect on the boiling point temperature which is measured inside the thermometer well.

The ebulliometer is 3 ft high and the condenser constitutes half of this height. The outlets J (letters refer to Figure 3), which are the connections to the magnetic pump, are 1 1/2" apart and are actually horizontally parallel. If flexible tubing is used to connect the ebulliometer to the pump (as was the case), the distance between the two legs is not critical.

The boiler is 1" in diameter and the inner tube has an ID of 1/4". The thermometer well has an ID of 1/2" and the Cotrell tubes are 6 mm in ID. The encasement is 2" in diameter and the condenser has a diameter of 1 1/2". The septum used was rubber on one side and Teflon on the other and had a diameter of 11 mm. The septa were purchased from Supelco, Inc. (Catalog no. 2-2731). The splash guard, C, guided the boiling liquid onto the thermometer well spiral. The ground glass fused in the boiling section was 30 mesh and this small size enhanced the boiling characteristics and thus the performance of the ebulliometer.

Except for the condenser, which was available commercially, the ebulliometer was assembled by the local glass-blower, Mr. M. Wayne Adkins, including the skillful fusing of the crushed glass to the inside wall of the boiler.

Approximately 5 ft of nichrome ribbon with a resistance of about 17 ohms was wrapped around the boiler in a helix. The ends of the wire were connected through alligator clips to a powerstat. The thermometer well was filled with silicon oil to provide good thermal contact between the thermometer well walls and the thermometer probe.

Vane-Type Magnetic Pump

The vane-type pump, Figure 7, is made of brass, is cylindrical in shape, and has a diameter of 35 mm and a height of 15 mm. Inside the pump there is a cylindrical aluminum block, C, in which two rectangular stainless steel vanes, E, are inserted symmetrically. The vanes are 9 mm by 16 mm, and are mutually in contact with two brass "push" rods, D, which are 18 mm in length and 1 mm in diameter. These rods are located horizontally near the top and the bottom of the aluminum block. The magnet, H, is inside the rotor which is mounted slightly off center in the brass housing, F. There is a 5 mm thick Teflon gasket, B, between the top and the body, F, of the pump. The pump is driven by a horseshoe magnet which is 2" x 1 1/2" x 1 1/2" and is mounted on a 0.01 hp motor connected to a powerstat. When the magnet turns, it rotates the cylindrical block inside the pump. The centrifugal force (and the push

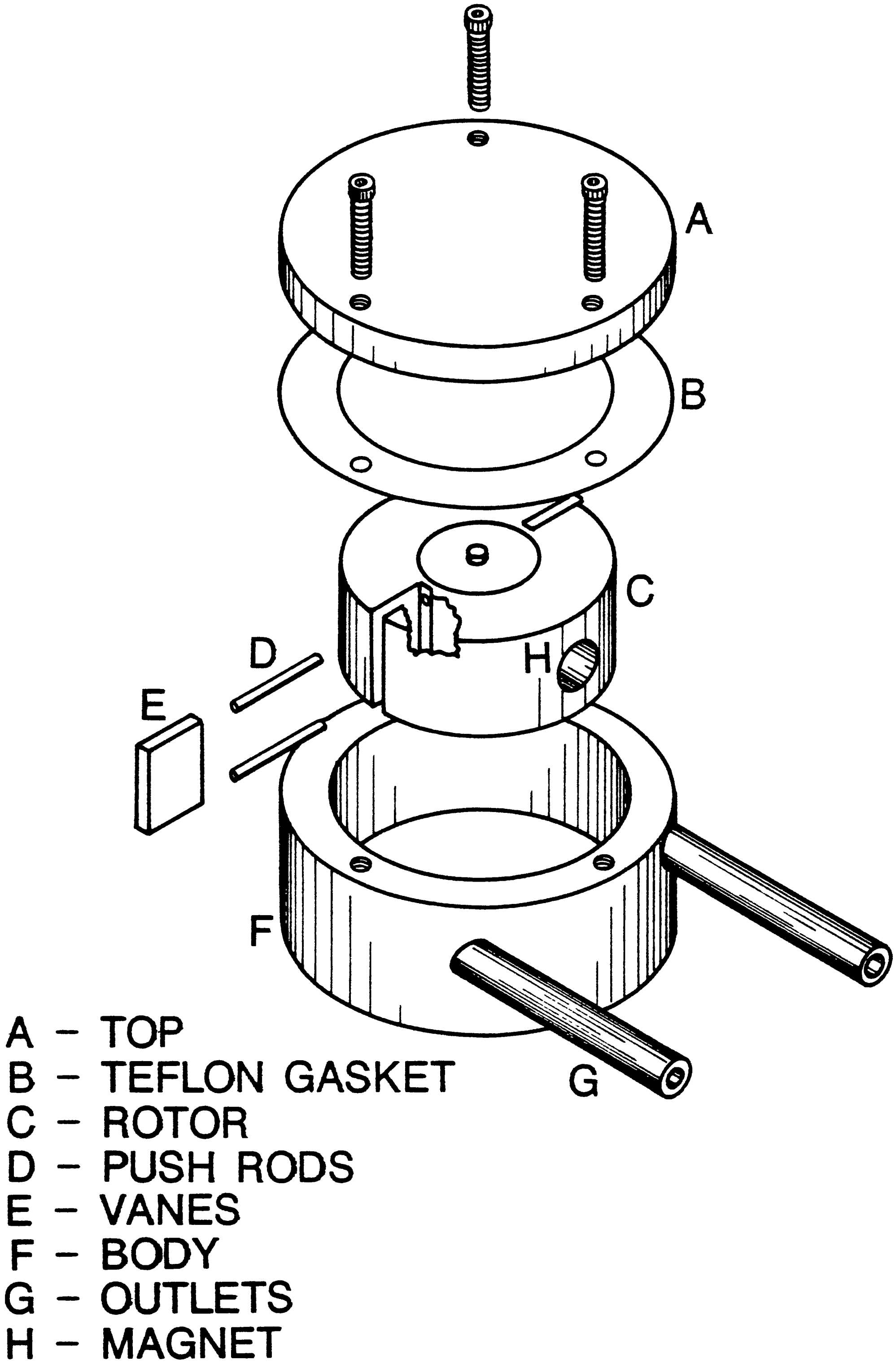


Figure 4. Magnetic Pump

rods) drive the vanes out to the wall of the pump and force the fluid to circulate in the manner typical of vane-type pumps. The pump outlets, G, are 5 mm in diameter and 35 mm long. The vane-type magnetic pump was fabricated by Mr. Heinz Hall at the Machine Shop of the Physics Department at Oklahoma State University.

The addition of the magnetic pump improved the performance of the ebulliometer considerably; this can be seen from temperature profiles shown in Figures 5 and 6. These figures demonstrate the boiling point temperature fluctuations of pure n-hexane at 170.53 mm Hg. The thermometer was in the differential mode and the difference in the boiling point of pure hexane in two ebulliometers was measured and recorded. The smallest divisions on the chart paper represent temperature changes of 10^{-3} °C. The chart-recorder speed was 15 mm/min. The temperature changes in Figure 5 are on the order of 2 x 10^{-2}°C and those in Figure 6 are on the order of 3 x 10^{-3}°C.

The Quartz Thermometer

Two ebulliometers are used in differential ebulliometry. One of them contains the pure solvent only and is called the reference ebulliometer. The other one is called a loading ebulliometer. The solute is injected into the loading ebulliometer.

The temperature difference between the reference ebulliometer and the loading ebulliometer was measured by a Hewlett-Packard Quartz Thermometer (Model 2804A) with matching sensor probes capable of resolution to 10^{-4}°C; however, only the medium resolution (10^{-3}°C) range was used in this work. The probes can be calibrated using either the triple point or freezing point of water. Calibrations were carried out

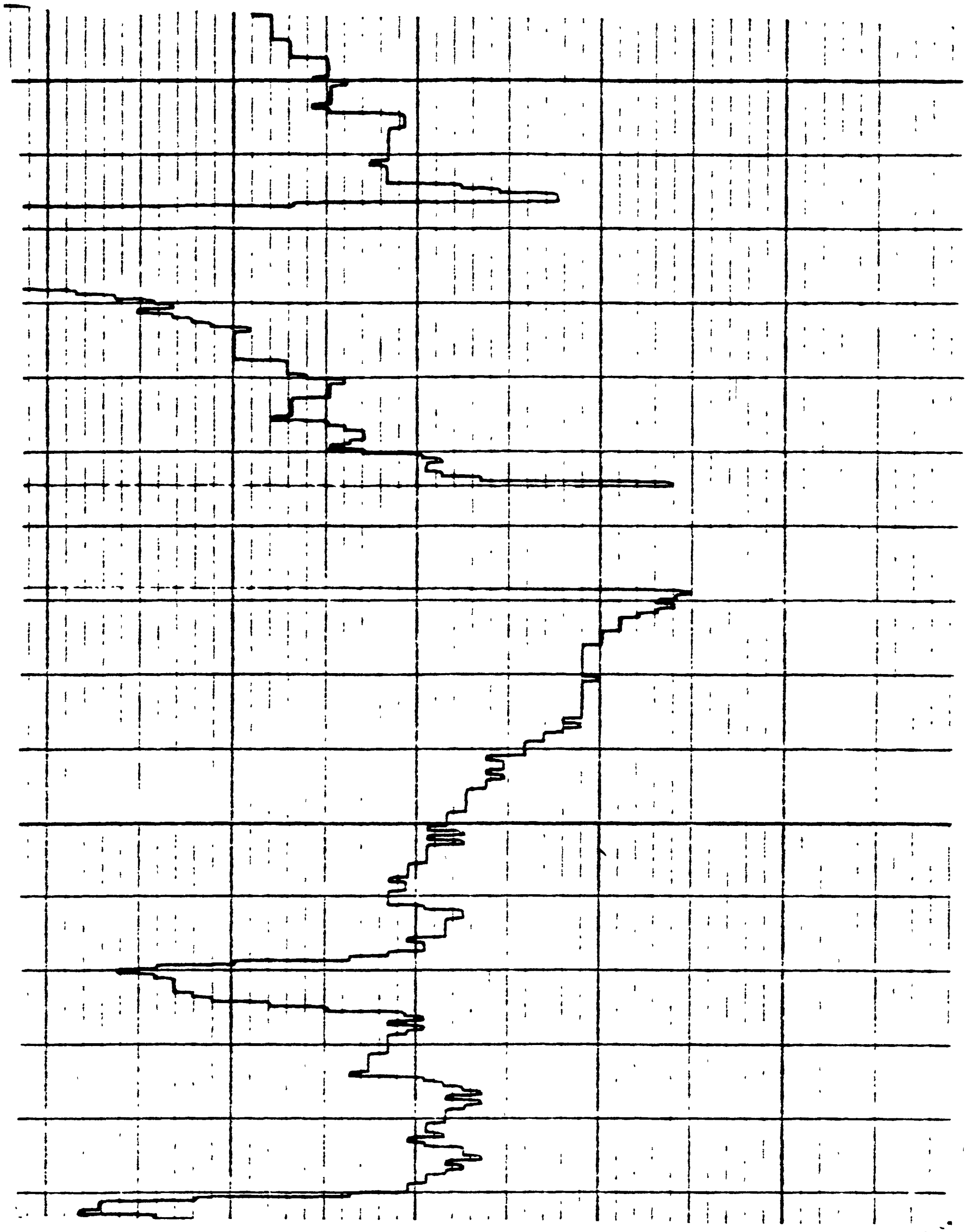


Figure 5. Temperature Fluctuations without the Magnetic Pump

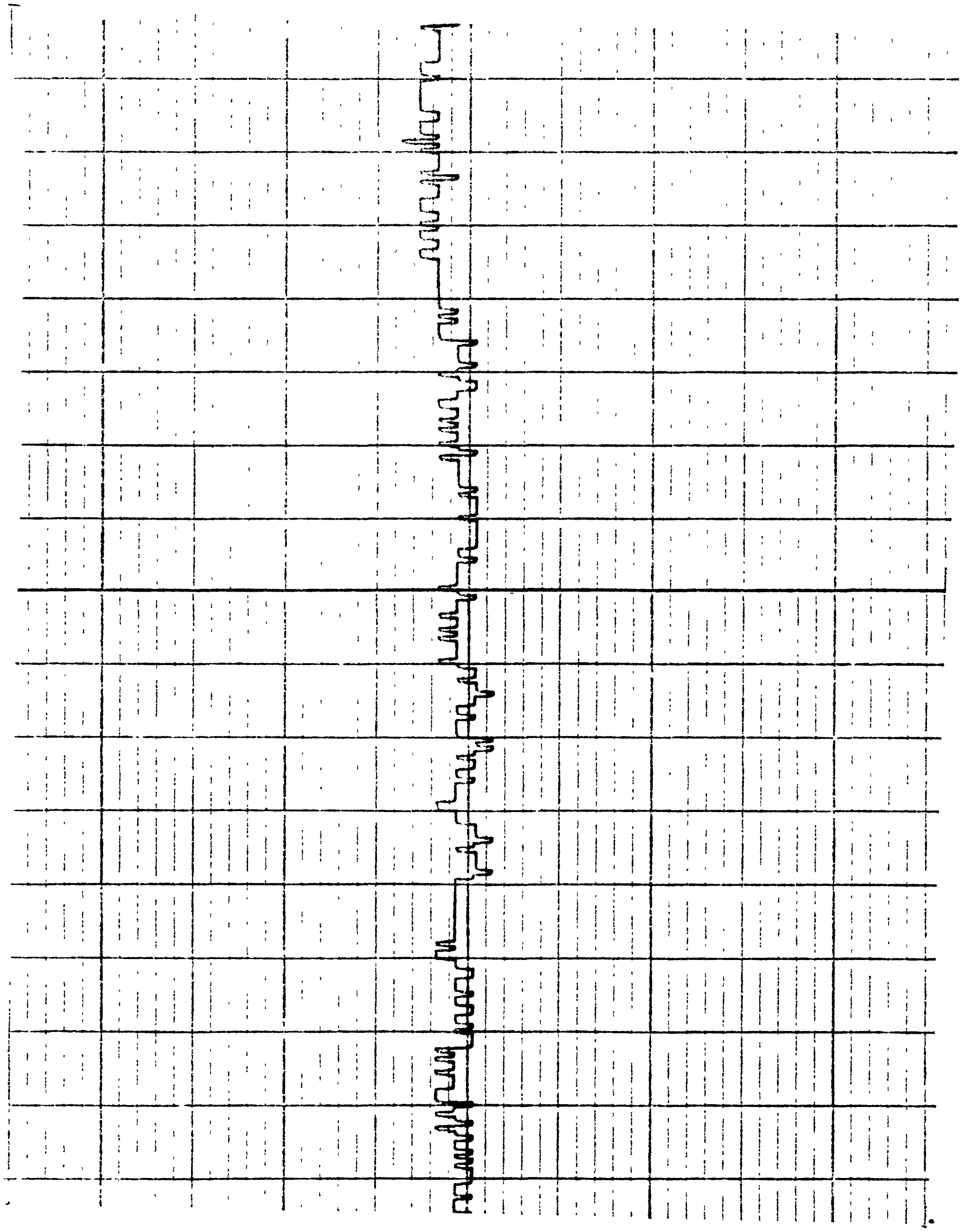


Figure 6. Temperature Fluctuations with the Magnetic Pump

in an ice bath in this work. When measuring the boiling point of the pure solvent in the two ebulliometers, both probes should read the same value of temperature. However, due to unmatched probes this difference was usually other than zero; it was read and recorded and subsequently subtracted from other readings. Typical values of this difference in reading were between 0.100 °C and 0.200°C with an average value of 0.150°C.

The probes are 23 cm long and have a maximum diameter of 11 mm. The probes can be used as far as 22 ft away from the thermometer read-out. They are very fragile and sensitive to shock and should be handled with extreme care. An 8" drop onto a hard surface will damage the probes permanently.

The absolute accuracy of the digital thermometer is $\pm 4\times10^{-2}$°C over the range of -50°C to 150°C. The digital display is pushbutton controlled and there is an internal switch where one can select the readings either in the Celsius or the Fahrenheit temperature scale.

Thumbwheel switches on the front panel can be used to adjust the probes by calibration against the ice point or triple point of water and thus the effects of thermal history on the sensor can be corrected. The thermometer can display the reading of either probe or show the difference between the two readings (differential mode). Three levels of resolution (low, medium, and high) are avilable. The time between display of readings depends on the resolution and mode selected, and ranges from 0.1 second for low resolution and absolute temperature to 20 seconds for high resolution and differential temperature. The overall range of the thermometer is from -80°C to 250°C.

There is an analog output option available on the Quartz Thermometer. The analog output is a d.c. voltage ranging from 0.00 to 9.99 volts and corresponds directly to the value of the selected digits. The desired digits can be selected on the front panel and can be any of the seven digits in display (XXX.XXXX). The analog output is delivered at the rear panel and can be used as input to a recording device.

Pressure Controller

A Texas Instrument Precision Pressure Test Set (Model 156) was used to control the pressure. This unit is capable of both reading and regulating pressures. The desired use can be switch-selected at the front panel. The operation of the Test Set is based upon the output of a fused quartz Bourdon capsule. In the Model 156, an absolute Bourdon capsule is installed.

There are three different modes of operation available: Manual Gage, Servo Gage, and Servo Control. In the present study only the Servo Control mode was used. In this mode the counter reading was manually adjusted to correspond to the desired controlled pressure. The error signal from the amplifier drives a pressure regulator. The regulator output pressure is connected to the Bourdon Capsule and the Regulated Pressure Output fitting.

The plumbing at the back of the Test Set consists of three fittings. The first fitting was connected to about 1 ft of stainless steel tubing and then through a vacuum hose to a vacuum pump. The second fitting was connected in a similar manner to the pressure supply source. The third fitting was connected directly to the Bourdon capsule and contained the regulated pressure. This fitting was connected to the manifold.

The pressure supply can be dry air, nitrogen or any other equivalent inert gas. In the present work nitrogen was used. The pressure at the pressure supply source should be 1.2 times the desired regulated pressure and should be set using a pressure regulator at the output of the gas tank.

The pressure range of the Test Set is from 0 to 1000 mm Hg and the control accuracy, i.e., the regulated pressure output versus counter reading is 0.002% of full scale (or 0.02 mm Hg in the present case).

The deviation meter at the front panel indicated pressure fluctuations in the range of 0.2 to 0.4 mm Hg with an average deviation of 0.3 mm Hg. This corresponded to a maximum temperature fluctuation of 1×10^{-4}°C in this work.

The Test Set is capable of providing output signals at the rear panel for recording purposes, but this feature of the Test Set was not used in the present work.

Circulating Bath

An Endocal Model RTE-4 Refrigerated Bath Circulator was used to provide coolant to the condenser. This unit can operate between -30°C to 100°C with a ±0.01°C temperature stability when water is used as the coolant. It has a 5 liter reservoir. When temperatures below 0°C are desired, a coolant such as ethylene-glycol or ethanol should be mixed in with water to prevent any freezing in the lines.

The unit is equipped with a circulating pump, proportional temperature controller and stainless steel refrigeration coils. The circulator was connected by 3/8" tygon tubing to the two ebulliometer condensers in series.

Vacuum Pump

A Sargent-Welch duo seal vacuum pump (Model 1400) was used. The vacuum pump was connected through ½" vacuum tubing to a cold trap which was in turn connected to the vacuum supply port of the pressure controller. The cold trap was not used since no vapor escaped the system.

Manifold

The two ebulliometers were connected through their condensers to a manifold using sealed glass ball joints, "O" ring seals, and pinch clamps. The regulated pressure was connected to the top of the manifold through a needle valve. The glass manifold has a diameter of 3" and a length of 18". The manifold was used to provide a large volume of inert gas and thus to dampen pressure fluctuations.

Chart Recorder

A Perkin-Elmer Model 561 Recorder was used to record the measured temperature differences. The Model 561 is a straight line potentiometric self-balancing Recorder with stepper motor chart drive. It has chart speeds ranging from 15 to 480 mm/min. It has zero adjust control and an effective chart width of 25 cm. The input voltage is either 0-10 mv or 0-1 v. Therefore, the output signal from the thermometer was reduced by a factor of 10 using a 56 kΩ and a 6.8 kΩ resistor in series, to match the recorder input voltage requirement.

Chemicals Used

The ethanol (supplied by U.S. Industrial Chemicals Co.) used in this work was 200 proof and was purchased locally. The other chemicals had minimum purities of 99 mole percent and were purchased from Aldrich Chemical Company, Inc. All the chemicals were used without any further purification.

Arrangement of Apparatus

The ebulliometers were clamped to an aluminum rod frame and connected through their condensers to the manifold. The quartz thermometer probes were inserted into the silicon oil in the thermometer wells.

The magnetic pumps were connected to the ebulliometer outlets using thick-walled tygon tubing which would not collapse under vacuum. The regulated pressure line of the pressure controller was connected to the manifold. The pressure supply and the vacuum supply were connected to the controller. The recorder was connected to the quartz thermometer at the rear panel. The magnetic pumps were positioned on the horse shoe magnet assembly. Alligator clips were attached to the nichrome wire heaters on the ebulliometers. The four powerstats were connected to the heating elements and the drive magnet motors.

CHAPTER IV

EXPERIMENTAL PROCEDURE

Cleaning the Ebulliometers

The ebulliometers were cleaned using acetone which was pumped through the Cotrell tubes. The acetone was heated slightly so that its vapor would condense inside the condenser and clean that area, too. The acetone was then drained and nitrogen gas at about 20 psia was used to evaporate any remaining acetone from the ebulliometers.

When the ebulliometers became discolored by metallic residue from the aluminum rotors of the magnetic pumps accumulating on the inside walls, the pumps were disconnected and concentrated nitric acid was used to remove the residue. The outlets J(in Figure 3) of the ebulliometers were connected to each other using tygon tubing when the pumps were removed.

Since the ebulliometers were connected to the manifold and were closed at the top, the acetone or other cleaning agents were loaded by removing the septum and pouring the liquid into the ebulliometers through a plastic funnel.

Charging the Solvent

Approximately 110 cc of the solvent was poured into a plastic bottle and weighed on a 0-100 g analytic balance capable of reading the mass to 10^{-4} g. Since all 110 cc could not be weighed at once using this balance, the process was carried out in two steps. After the liquid had been poured into the loading ebulliometer, the "empty" container was weighed and the mass of the "empty" bottle was subtracted from the mass of the full bottle to determine the exact mass of solvent charged.

The exact mass of the solvent charged to the reference ebulliometer did not need to be determined. 110 cc of solvent was poured into the reference ebulliometer without weighing.

Pressure Regulation

After the solvent had been charged, the selected pressure was set on the pressure regulator (using the calibration chart supplied by Texas Instruments). The pressure supply was connected and a pressure 1.2 times the selected value was supplied using the gas tank regulator. The vacuum pump was turned on, the needle valve at the manifold was opened, and the pressure was allowed to reach a stable value as indicated by the deviation meter on the Pressure Test Set. An average deviation of 0.30 mm Hg was considered satisfactory. The pressure fluctuations were very slow at low pressures (150 mm Hg) and rather fast at high pressures (700 mm Hg). Pressure fluctuations were dampened by the ballast in the manifold.

Temperature Measurement and Recording

When the pressure stabilized, the magnetic pumps were turned on and set at a sufficiently high flow rate to wet the thermometer well completely. At this point heating was initiated. The voltage selected depended on the resistance of the nichrome wire used as the heating element. In the present study, the powerstat voltage was set at 35 in order to achieve a boiling point temperature of about 80°C, using a 17Ω resistance.

Once boiling had started and vapor bubbles could be seen in the Cotrell tubes, the temperature was allowed to stabilize in both ebulliometers. The temperature difference between the two ebulliometers when both contained pure solvent (which was close to zero) was read. The temperature differences were recorded for about 40 minutes to make sure that the equilibrium temperature had been reached. A fluctuation of about 5×10^{-3}°C was considered satisfactory; when this level of performance was observed, preparations were made for the first injection. The liquid level in the ebulliometer was observed to be constant when steady state had been reached. The boiling was usually very vigorous and the condensation ring could be seen in the condenser. If periodic fluctuations in the level were observed, temperature stability was not achieved.

Solute Injections

At this point about 1 cc of the solute was drawn into a syringe. The syringe was weighed, then the solute was injected through the Teflon septum into the loading ebulliometer. The syringe was immediately reweighed and the exact mass of solute injected was determined. The change in the boiling point temperature was noted and when the temperature reached a new steady state value, the recorder (which had been turned off before the injection) was turned back on and the temperature fluctuations were recorded for about 20 minutes. Again, fluctuations were typically on the order of 0.005°C. The new boiling point temperature was recorded. A total of 4 or 5 injection was made in a similar manner, and each time the temperature fluctuations were monitored and recorded. The heating was then stopped and the pressure controller was disconnected from the manifold by closing the needle valve. Once the pressure controller, the vacuum pump, the pressure supply and the magnetic pumps were turned off, the ebulliometers were drained and cleaned. The thermometer could be switched off at any time with probes remaining in the thermometer wells.

Each experimental run took about 4 hours and the stabilization of the pressure and temperature took place faster at lower pressures. However, the boiling did not appear as vigorous at lower pressures as it did at higher pressures.

CHAPTER V

DATA REDUCTION

Since there was condensed vapor holdup in the condenser, liquid holdup in the condenser and on the glass spiral, and vapor holdup in the space between the boiling liquid and the condensing vapor in the ebulliometer, the compositions obtained using the charged masses of liquid needed to be corrected. The procedure for making these corrections and reducing data follows.

The overall mole fraction, z_1, of the solute in the ebulliometer was calculated as follows.

$$z_1 = \frac{n_1}{n_1 + n_2} \tag{13}$$

However, z_1 in the above equation is the "overall" mole fraction and is not equal to the liquid mole fraction when any vaporization takes place in the ebulliometer. After boiling begins, some vapor and liquid "holdup" must be taken into account to obtain the liquid composition. When z_1 in the above equation is corrected for vapor and liquid holdups, the corrected liquid mole fraction is referred to as x_1.

The data obtained experimentally in this work were corrected for vapor and liquid holdups; a computer program (Appendix A) was used to make the corrections (using the following concepts).

The ebulliometer was envisioned to consist of four sections. The first section consisted of the liquid volume during the experimental run. The second section was the volume of the liquid held up on the thermometer well spiral. The third section was the volume of the condensed vapor in the condenser. The fourth section was the vapor volume through the rest of the ebulliometer. These volumes were designated by V_z^L, V_x^L, V_y^L, and V_y^V, respectively. The value of V_z^L was known to be approximately 106 cc. The values of V_y^L, V_y^V, and V_x^L were estimated to be 2 cc, 200 cc, and 2 cc, respectively. In order to calculate the vapor composition (mole fraction), equilibrium ratios were needed. These were calculated using the following relationships:

$$K_i = \frac{y_i}{x_i} \tag{14}$$

K_i = equilibrium ratio of component "i"

y_i = vapor mole fraction of component "i"

x_i = liquid mole fraction of component "i"

$$\hat{f}_i^V = \hat{f}_i^L \quad \text{(equilibrium criteria)} \tag{15}$$

$$\hat{f}_i^V = y_i \; \hat{\phi}_i \; P \tag{16}$$

$$\hat{f}_i^L = x_i \gamma_i f_i^0 \tag{17}$$

$$y_i \hat{\phi}_i P = x_i \gamma_i f_i^0 \tag{18}$$

$\hat{\phi}_i$ = fugacity coefficient of component "i" in the mixture $(\hat{\phi}_i = \frac{\hat{f}_i^V}{y_i P})$

γ_i = activity coefficient of component "i" in the mixture $(\gamma_i = \frac{\hat{f}_i^L}{x_i f_i^0})$

f_i = fugacity of component "i"

P = total pressure

$$\text{but } f_i^0 = P_i^0 \phi_i^0 \tag{19}$$

$$y_i \hat{\phi}_i P = x_i \gamma_i P_i^0 \phi_i^0 \tag{20}$$

Solving the above equation for γ_i and taking logarithms:

$$\ln\gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \ln\hat{\phi}_i - \ln\phi_i^0 \tag{21}$$

At low pressures: $\ln \hat{\phi}_i = \ln\phi_i^0 = 1$ (22)

$$\gamma_i = \frac{y_i P}{x_i P_i^0} \tag{23}$$

$$K_i = \frac{y_i}{x_i} = \frac{P_i^0 \gamma_i}{P} \tag{24}$$

Now using the one constant Margules Equation for γ_i:

$$\ln\gamma_1 = Ax_2^2 = A(1 - x_1)^2 \tag{25}$$

$$\ln\gamma_2 = Ax_1^2 \tag{26}$$

and Equation (24) yields

$$K_1 = \frac{P_1^0}{P} \exp\,[A(1 - x_1)^2] \tag{27}$$

$$K_2 = \frac{P_2^0}{P} \exp\,(Ax_1^2) \tag{28}$$

Here P_1^0 and P_2^0 are the vapor pressures of the solute and solvent, respectively. The vapor pressure of the solvent, when the solute is infinitely dilute, is the same as the operating pressure of the system and was known experimentally. The vapor pressure of the solute was calculated using the three constant Antoine Equation:

$$P_i^0 = P_{Ci} \exp\left[A_1 - \frac{A_2}{A_3 + T'}\right]$$

where P_i^0 is the saturated vapor pressure of component "i" in psia and P_{Ci} is the critical pressure of the same component in psia. T' is the boiling point temperature in °F.

The Margules constant A is calculated using Equation (25) for the infinitely dilute case ($x_1 = 0$):

$$A = \ln\gamma_1^\infty \tag{29}$$

γ_1^∞ in the above equation is calculated using Equation (12). In that equation, P_2^0 is the solvent vapor pressure and was measured directly. $\frac{dP_2^0}{dT}$ was calculated by differentiating the Antoine Equation with respect to temperature:

$$\frac{dP_2^0}{dT} = P_2^0\left[\frac{A_2}{(A_3 + T')^2}\right] \tag{30}$$

The mole fraction versus the boiling point temperature curves were nearly linear over the composition ranges studied, however, there was a slight curvature in some of them. Therefore, both linear and quadratic fits to the experimental data were used, i.e.,

$$\Delta T = ax_1 \tag{31}$$

and

$$\Delta T = ax_1 + bx_1^2 \tag{32}$$

The slope of either of these curves at infinite dilution ($x_1 = 0$) is

$\frac{d(T)}{dx_1} = a$. The constants in Equations (31) and (32) were calculated by minimizing the sum of the squares of errors:

$$SS = \Sigma\,(T_{\text{measured}} - T_{\text{calculated}})^2 \tag{33}$$

where the summation extends over all $\Delta T - x_1$ points in a given experiment. This leads to

$$a = \frac{\Sigma\; x_i \Delta T_i}{\Sigma\; x_i^2}\text{, for the linear case} \tag{34}$$

$$a = \frac{\Sigma\, x_i \Delta T_i - b\; \Sigma\, x_i^3}{\Sigma\, x_i^2}\text{, for the quadratic case} \tag{35}$$

where

$$b = \frac{[(\Sigma\, x_i \Delta T_i) - (\Sigma\, x_i^2 \Delta T_i)(\Sigma\, x_i^2)]/(\Sigma\, x_i^3)}{(\Sigma\, x_i^3) - [(\Sigma\, x_i^4)(\Sigma\, x_i^2)/(\Sigma\, x_i^3)]} \tag{36}$$

As a first approximation, the overall mole fraction z_i was used (instead of x_i) to get "a" from both (34) and (35). This value of "a" corresponds to the $\frac{dT}{dx_1}$ term and permits the calculation of γ_1^∞ by Equation (12). From γ_1^∞, the Margules constant was calculated using Equation (29). The Margules constant was then used to calculate K_1 and K_2 from Equations (27) and (28). This permitted the calculation of y_1, the vapor mole fraction of the solute using:

$$y_i = K_i x_i \tag{37}$$

The following molar material balances were then used to correct z_i and obtain x_i:

$$n_1 = n_{10} - n_y^L y_1 - n_y^V y_1 \tag{38}$$

$$n_2 = n_{20} - n_y^L(1 - y_1) - n_y^V(1 - y_1) \tag{39}$$

where n_{10} and n_{20} are the number of moles of the solute and solvent charged to the cell, and n_1 and n_2 are the corrected liquid phase values after some of the solvent and solute have vaporized.

Using the product of the density and volume to give the number of moles in Equations (38) and (39), i.e.,

$$n = \rho V \tag{40}$$

Then

$$n_1 = n_{10} - [\rho^L V_y^L + \rho^V V_y^V]y_1 \tag{41}$$

$$n_2 = n_{20} - [\rho^L V_y^L + \rho^V V_y^V](1 - y_1) \tag{42}$$

The vapor densities were calculated using the ideal gas law, since the pressures were low enough to warrant its use. Also, the magnitude of the value of the vapor density was very small compared to the liquid density, and its effect in the material balance equations was minimal. Thus,

$$\rho^V = \frac{P}{RT} \tag{43}$$

The liquid densities of the pure components were calculated using the Rackett Equation (30):

$$\frac{1}{\rho^L} = v^L = 83.147 \left(\frac{T_c}{P_c}\right) A^{[1 + (1 - \frac{T}{T_c})]^{0.2857}} \tag{44}$$

ρ^L = liquid density in gmol/cm^3

v^L = liquid specific volume in cm^3/gmol

T_c = critical temperature in K

T = boiling temperature in K

P_c = critical pressure in atm

A = Rackett Equation Constant

The density of the mixture was calculated assuming ideal mixing as follows:

$$v^L_{mixture} = x_1 v_1{}^L + (1 - x_1) v_2{}^L \tag{45}$$

$$\rho^L_{mixture} = \frac{1}{v^L_{mixture}} \tag{46}$$

The values of the contants in the above equation and all other constants used in calculations are given in Appendix C.

New mole fractions were then calculated using the following equations:

$$x_1 = \frac{n_1}{n_1 + n_2} \tag{47}$$

$$x_2 = 1 - x_1 \tag{48}$$

At this point a convergence criterion was checked and if the new and old values of x_i agreed within a specified tolerance (10^{-4}), the calculations for x_i were stopped. Otherwise, the above procedure was repeated until the convergence condition was satisfied, i.e., x_i were used in Equations (34) and (35) to get "a" and "b", "A" was calculated using Equation (29), K_i were calculated using Equations (27) and (28), y_i were calculated using Equation (37), and new x_i were calculated using Equations (41), (42), (47) and (48). Once the corrected values of the liquid mole fraction were known, the correct infinite dilution activity coefficient was obtained.

CHAPTER VI

EXPERIMENTAL RESULTS AND DISCUSSION

Experimental Results

The experimental results from this study are presented in Tables I through VII. In these tables, the components are labeled by "1" for solute and "2" for solvent. Next, the operating pressure of the system is specified followed by the boiling temperature of the pure solvent and the mass in grams of the solvent charged.

In the first column, the mass of the solute added in grams is indicated. In the second column, the uncorrected (overall) mole fraction is recorded. These mole fractions were calculated in the following manner:

$$n_1 = \frac{m_1}{MW_1} \tag{49}$$

$$n_2 = \frac{m_2}{MW_2} \tag{50}$$

$$x_1 = \frac{n_1}{n_1 + n_2} \tag{51}$$

The third column gives the experimental change in the boiling point temperature corresponding to each solute mole fraction. The calculated values of the change in the boiling point temperature based on the linear and quadratic fits are presented in columns four and five. In the fifth and sixth columns, the linearly and quadratically fitted values of the corrected solute mole fraction are recorded.

All tables are based on the point $x_1 = 0$, $\Delta T \doteq 0$, i.e., the initial ΔT reading from the thermometers before any solute was added has been subtracted from the subsequent readings. Each table contains three sets of data obtained at three operating pressures for the same binary system.

The final calculated results are shown in Table VIII. The binary system is specified in the first column. The operating pressure is indicated in the second column. The boiling point temperature of the pure solvent is given in the third column. The linearly and quadratically fitted values of the infinite dilution activity coefficient are presented in columns four and five. The γ_1^{∞} values of Eckert et. al are given in column six.

The effects of temperature on infinite dilution activity coefficient are shown in Figures 7 through 13. Each figure contains three data points representing the three pressures at which the binary system data were obtained. Error bars of ±1% are shown on each figure, except Figure 4 where they would cover the entire figure. These figures are a measure of the linearity of the experimental data. Error bars take into account the non-linearity that might have been introduced by experimental errors. These figures show that the data are consistent. Most plots are linear if the experimental uncertainty is taken into account.

Figures 14 through 20 show typical isobaric boiling point results. These figures correspond to the intermediate pressures at which the experiments were conducted. These plots show the effect of

TABLE I

ISOLARIC BOILING POINTS FOR TOLUENE (1)-ETHANOL (2) MIXTURES

Solute Added, m_1 (gm)	Overall Mol. Frn., z_1	Boiling Pt. Change, ΔT(°C)	Error in Calcd. ΔT(°C)		Calcd. Liquid Comp., x_1	
			Linear	Quadratic	Linear	Quadratic
P = 705 mm Hg, $T_{b,\ solvent}$ = 76.364°C, m_2 = 81.444 gm						
1.173	0.00716	-0.150	-0.01283	-0.00180	0.00703	0.00703
2.387	0.01446	-0.290	-0.01256	-0.01256	0.01422	0.01422
3.227	0.01974	-0.382	-0.00284	-0.00284	0.01943	0.01943
4.212	0.02524	-0.472	+0.01303	+0.01303	0.02486	0.02486
P = 310 mm Hg, $T_{b,\ solvent}$ = 56.815°C, m_2 = 83.955 gm						
1.040	0.00617	-0.144	-0.01149	-0.01149	0.00604	0.00603
2.088	0.01230	-0.279	-0.01426	-0.01426	0.01207	0.01207
3.313	0.01938	-0.423	-0.00535	-0.00535	0.01904	0.01900
4.526	0.02586	-0.554	-0.01328	+0.01328	0.02586	0.02581
P = 180 mm Hg, $T_{b,\ solvent}$ = 45.901°C, m_2 = 76.323 gm						
1.3267	0.00781	-0.225	-0.02755	-0.00350	0.00763	0.00760
2.5342	0.01481	-0.406	-0.03088	-0.00002	0.01450	0.01445
3.8790	0.02249	-0.591	-0.02035	+0.00170	0.02206	0.02199
4.9128	0.02831	-0.722	-0.00274	+0.00118	0.02780	0.02772
6.2798	0.03591	-0.880	+0.03350	-0.00123	0.03531	0.03521

TABLE II

ISOBARIC BOILING POINTS FOR CYCLOHEXANE (1)-BENZENE (2) MIXTURES

Solute Added, m_1 (gm)	Overall Mol. Frn., z_1	Boiling Pt. Change, ΔT(°C)	Error in Calcd. ΔT(°C)		Calcd. Liquid Comp., x_1	
			Linear	Quadratic	Linear	Quadratic
P = 669 mm Hg, $T_{b,\ \text{solvent}}$ = 75.507°C, m_2 = 92.482 gm						
1.216	0.01196	-0.163	-0.01808	-0.01201	0.01185	0.01185
2.306	0.02243	-0.271	+0.00104	+0.00737	0.02225	0.02224
3.354	0.03230	-0.391	+0.00084	+0.00310	0.03204	0.03204
4.497	0.04283	-0.516	+0.00387	+0.00285	0.04251	0.04251
P = 418 mm Hg, $T_{b,\ \text{solvent}}$ = 61.776°C, m_2 = 90.135 gm						
1.029	0.01052	-0.150	-0.00758	-0.00018	0.01042	0.01041
1.989	0.02014	-0.280	-0.00725	+0.00119	0.01995	0.01994
3.044	0.03049	-0.418	-0.00478	-0.00136	0.03022	0.03020
4.162	0.04123	-0.550	+0.00900	+0.00047	0.04089	0.04086
P = 193 mm Hg, $T_{b,\ \text{solvent}}$ = 41.386°C, m_2 = 90.619 gm						
1.044	0.01061	-0.162	-0.00524	+0.00286	0.01049	0.01048
2.077	0.02088	-0.321	-0.01218	-0.00331	0.02066	0.02064
3.093	0.03079	-0.451	-0.0151	-0.00150	0.03045	0.03045
4.105	0.04045	-0.590	+0.00881	-0.00019	0.04003	0.04003

TABLE III

ISOBARIC BOILING POINTS FOR BENZENE (1)-CYCLOHEXANE (2) MIXTURES

Solute Added, m_1 (gm)	Overall Mol. Frn., z_1	Boiling Pt. Change, ΔT(°C)	Error in Calcd. ΔT(°C) Linear	Error in Calcd. ΔT(°C) Quadratic	Calcd. Liquid Comp., x_1 Linear	Calcd. Liquid Comp., x_1 Quadratic
P = 727 mm Hg, $T_{b,solvent}$ = 78.690°C, m_2 = 79.545 gm						
1.348	0.01549	-0.228	-0.02103	-0.01025	0.01535	0.01534
2.505	0.03138	-0.411	-0.00332	+0.00817	0.03112	0.03109
3.418	0.04553	-0.537	-0.00346	-0.00021	0.04512	0.04512
4.687	0.05841	-0.709	+0.01005	-0.00151	0.05798	0.05798
P = 389 mm Hg, $T_{b,\ solvent}$ = 59.874°C, m_2 = 84.649 gm						
1.360	0.01701	-0.226	-0.00294	+0.00249	0.01685	0.01685
2.246	0.02779	-0.371	-0.00651	-0.00108	0.02755	0.02754
3.311	0.04043	-0.534	-0.00340	-0.00140	0.04011	0.04010
4.504	0.05421	-0.705	+0.00679	+0.00082	0.05380	0.05379
P = 170 mm Hg, $T_{b,\ solvent}$ = 37.651°C, m_2 = 80.801 gm						
1.179	0.01696	-0.199	-0.01184	+0.00075	0.01696	0.01680
2.427	0.03107	-0.364	-0.01485	-0.00272	0.03107	0.03079
3.573	0.04192	-0.527	-0.00229	+0.00269	0.04192	0.04155
4.647	0.05661	-0.662	+0.01338	-0.00072	0.05661	0.05614

TABLE IV

ISOBARIC BOILING POINTS OF CYCLOHEXANE (1)-HEXANE (2) MIXTURES

Solute Added, m_1 (gm)	Overall Mol. Frn., z_1	Boiling Pt. Change, ΔT(°C)	Error in Calcd. ΔT(°C)		Calcd. Liquid Comp., x_1	
			Linear	Quadratic	Linear	Quadratic
P = 550 mm Hg, $T_{b,\ solvent}$ = 58.550°C, m_2 = 67.517 gm						
0.947	0.01612	0.112	+0.00046	-0.00004	0.01612	0.01623
2.053	0.03021	0.249	+0.00040	-0.00012	0.03021	0.03040
3.001	0.04289	0.357	+0.00041	+0.00021	0.04289	0.04315
3.906	0.05783	0.458	-0.00064	-0.00008	0.05783	0.05817
P = 300 mm Hg, $T_{b,\ solvent}$ = 41.924°C, m_2 = 69.547 gm						
0.860	0.01250	0.095	+0.00033	+0.00144	0.01250	0.01250
1.686	0.02422	0.182	-0.00253	-0.00115	0.02437	0.02437
2.770	0.03943	0.298	-0.00049	+0.00015	0.03943	0.03942
3.890	0.05417	0.414	+0.00141	+0.00008	0.05450	0.05449
P = 171 mm Hg, $T_{b,\ solvent}$ = 27.958°C, m_2 = 68.172 gm						
1.090	0.01422	0.115	-0.00330	-0.00292	0.01422	0.01623
2.074	0.03033	0.215	+0.00152	+0.00193	0.03052	0.03040
2.983	0.04372	0.305	+0.00028	+0.00040	0.04400	0.04315
4.086	0.05616	0.410	-0.00021	-0.00062	0.05652	0.05818

TABLE V

ISOBARIC BOILING POINTS OF HEXANE (1)-CYCLOHEXANE (2) MIXTURES

Solute Added, m_1 (gm)	Overall Mol. Frn., z_1	Boiling Pt. Change, ΔT(°C)	Error in Calcd. ΔT(°C)		Calcd. Liquid Comp., x_1	
			Linear	Quadratic	Linear	Quadratic
P = 700 mm Hg, T_b solvent = 77.963°C, m_2 = 83.973 gm						
0.684	0.00789	-0.131	+0.00686	+0.00399	0.00779	0.00789
1.374	0.01572	-0.271	+0.00482	-0.00090	0.01553	0.01554
2.202	0.02496	-0.436	+0.00047	-0.00238	0.02466	0.02467
3.097	0.03476	-0.612	-0.00407	+0.00120	0.03435	0.03437
P = 350 mm Hg, $T_{b,}$ solvent = 56.961°C, m_2 = 81.157 gm						
0.908	0.01081	-0.187	-0.00259	+0.00183	0.01081	0.01066
1.858	0.02187	-0.380	-0.00668	-0.00183	0.02187	0.02156
2.707	0.03155	-0.540	-0.00126	+0.00058	0.03155	0.03115
3.646	0.04203	-0.713	+0.00508	+0.00005	0.04203	0.04152
P = 150 mm Hg, $T_{b,}$ solvent = 35.045°C, m_2 = 80.547 gm						
0.988	0.01184	-0.204	-0.00567	-0.00030	0.01167	0.01184
2.298	0.02711	-0.460	-0.00550	+0.00012	0.02675	0.02674
3.195	0.03730	-0.627	-0.00142	+0.00016	0.03682	0.03680
4.105	0.04741	-0.790	-0.00567	-0.00012	0.04683	0.04681

TABLE VI

ISOBARIC BOILING POINTS OF BENZENE (1)-HEXANE (2) MIXTURES

Solute Added, m_1 (gm)	Overall Mol. Frn., z_1	Boiling Pt. Change, ΔT(°C)	Error in Calcd. ΔT(°C)		Calcd. Liquid Comp., x_1	
			Linear	Quadratic	Linear	Quadratic
P = 700 mm Hg, $T_{b,\text{ solvent}}$ = 66.095°C, m_2 = 72.653 gm						
1.141	0.01703	-0.020	-0.00704	-0.00124	0.01703	0.01703
2.157	0.03172	-0.027	-0.00287	+0.00127	0.03172	0.03172
3.309	0.04785	-0.032	+0.00441	-0.00040	0.04785	0.04785
P = 350 mm Hg, $T_{b,\text{ solvent}}$ = 45.920°C, m_2 = 69.785 gm						
1.267	0.01963	-0.016	-0.00291	-0.00187	0.01963	0.01963
2.498	0.03798	-0.027	-0.00168	-0.00061	0.03798	0.03798
3.738	0.05578	-0.034	-0.00319	+0.00339	0.05578	0.05578
4.708	0.06962	-0.047	-0.00083	-0.00186	0.06926	0.06926
P = 150 mm Hg, $T_{b,\text{ solvent}}$ = 24.950°C, m_2 = 66.729 gm						
1.341	0.02170	-0.035	-0.01186	-0.00219	0.02170	0.02170
2.559	0.04061	-0.052	-0.00869	+0.00111	0.04061	0.04061
3.724	0.05802	-0.064	-0.00211	+0.00096	0.05802	0.05802
4.948	0.07565	-0.071	+0.00969	-0.00071	0.07565	0.07565

TABLE VII

ISOBARIC BOILING POINTS OF HEXANE (1)-BENZENE (2) MIXTURES

Solute Added, m_1 (gm)	Overall Mol. Frn., z_1	Boiling Pt. Change, ΔT(°C)	Error in Calcd. ΔT(°C)		Calcd. Liquid Comp., x_1	
			Linear	Quadratic	Linear	Quadratic
P = 700 mm Hg, $T_{b,\ solvent}$ = 77.347°C, m_2 = 90.961 gm						
1.015	0.01001	-0.397	-0.01504	+0.00779	0.00973	0.00971
1.874	0.01832	-0.724	-0.02384	-0.00196	0.01785	0.01780
2.664	0.02585	-1.001	-0.01224	-0.00698	0.02520	0.02514
3.400	0.03277	-1.227	+0.02753	-0.00422	0.03197	0.03190
P = 350 mm Hg, $T_{b,\ solvent}$ = 56.642°C, m_2 = 91.055 gm						
0.962	0.00948	-0.412	-0.02375	-0.00198	0.00919	0.00916
1.797	0.01757	-0.743	-0.02255	+0.00127	0.01704	0.01700
2.581	0.02504	-1.040	-0.01170	+0.00033	0.02433	0.02427
3.684	0.03537	-1.429	+0.02577	-0.00034	0.03442	0.03435
P = 150 mm Hg, $T_{b,\ solvent}$ = 35.378°C, m_2 = 91.662 gm						
0.986	0.00966	-0.462	-0.02966	-0.00002	0.00931	0.00927
2.075	0.02011	-0.935	-0.03245	+0.00095	0.01943	0.01937
3.011	0.02892	-1.315	-0.01452	-0.00124	0.02800	0.02791
4.073	0.03873	-1.710	+0.03496	+0.00043	0.03757	0.03747

TABLE VIII

EXPERIMENTAL INFINITE DILUTION ACTIVITY COEFFICIENTS

			Infinite Dilution Activity Coefficient, γ_1^∞		
			This Work		Eckert (30)
Solute/Solvent	Pressure mm Hg	Temperature °C	Linear	Quadratic	
Tolune/Ethanol	705.38	76.364	4.91	5.22	5.14
	309.55	56.815	5.28	5.61	5.34
	180.00	45.901	5.88	6.23	5.60
Cyclohexane/Benzene	669.44	75.507	1.42	1.45	1.45
	417.50	61.776	1.48	1.52	1.52
	192.70	41.386	1.57	1.62	1.61
Benzene/Cyclohexane	726.70	78.690	1.37	1.40	1.35
	388.60	59.870	1.43	1.45	1.41
	169.50	37.651	1.50	1.54	1.48
Cyclohexane/Hexane	550.00	58.550	1.07	1.07	1.07
	300.00	41.924	1.06	1.07	1.09
	170.53	27.958	1.07	1.06	1.09
Benzene/Hexane	700.00	66.095	1.46	1.49	
	350.00	45.920	1.52	1.53	
	150.00	24.950	1.62	1.67	
Hexane/Benzene	700.00	77.347	1.59	1.68	
	350.00	56.642	1.76	1.85	
	150.00	35.378	1.92	2.05	
Hexane/Cyclohexane	700.00	77.963	1.08	1.14	
	350.00	56.966	1.10	1.11	
	150.00	35.045	1.12	1.06	

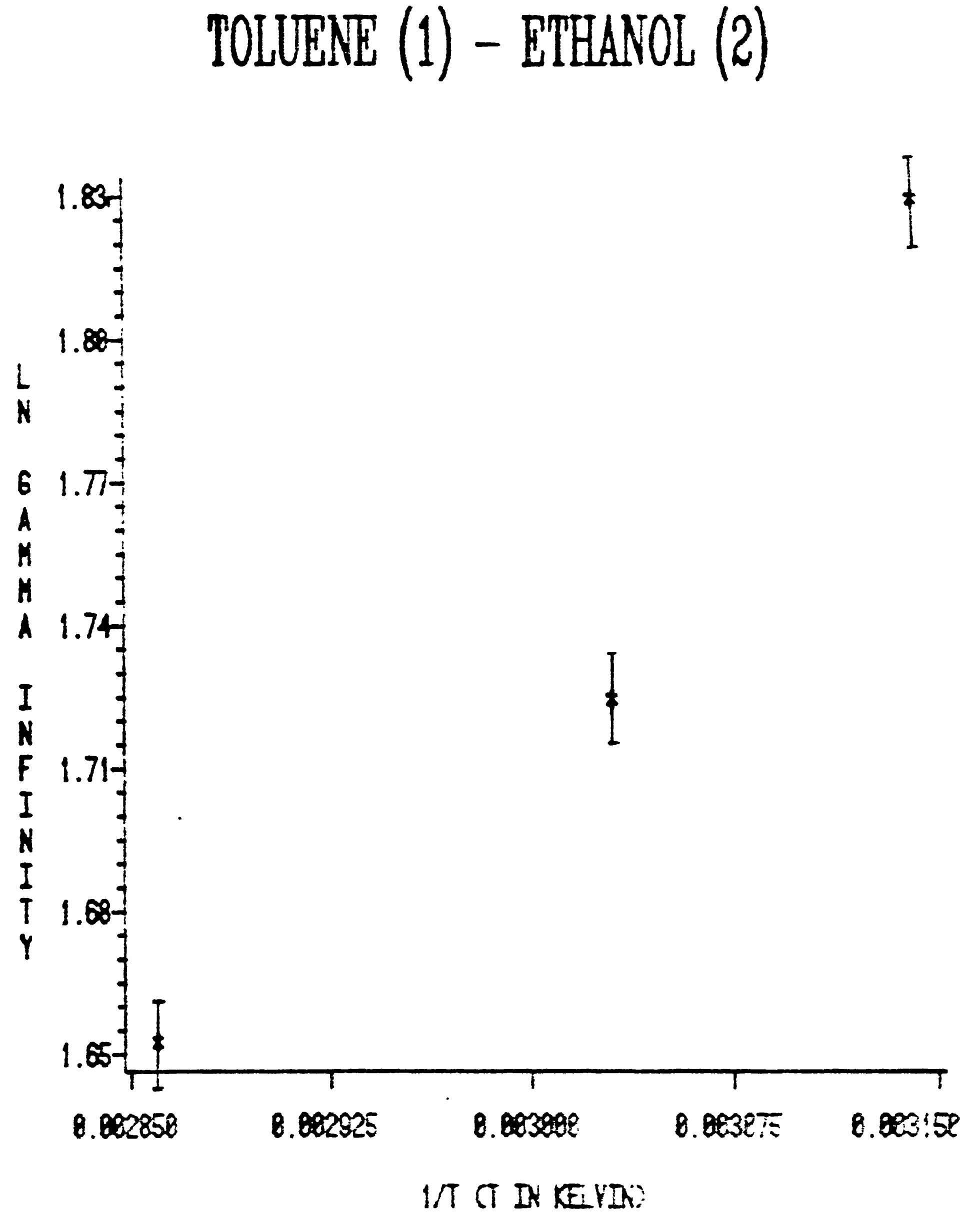


Figure 7. Infinite Dilution Activity Coefficient for Toluene in Ethanol

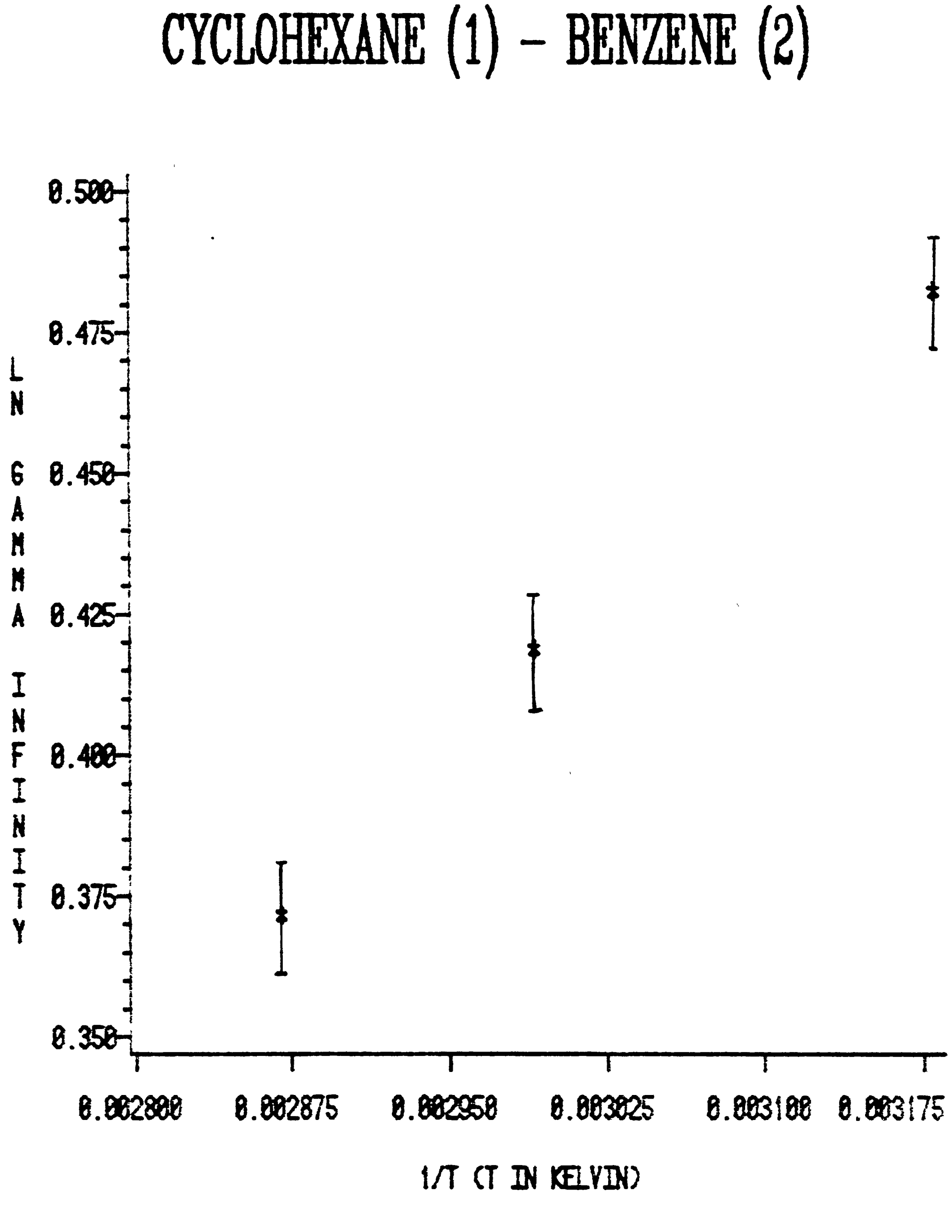


Figure 8. Infinite Dilution Activity Coefficient for Cyclohexane in Benzene

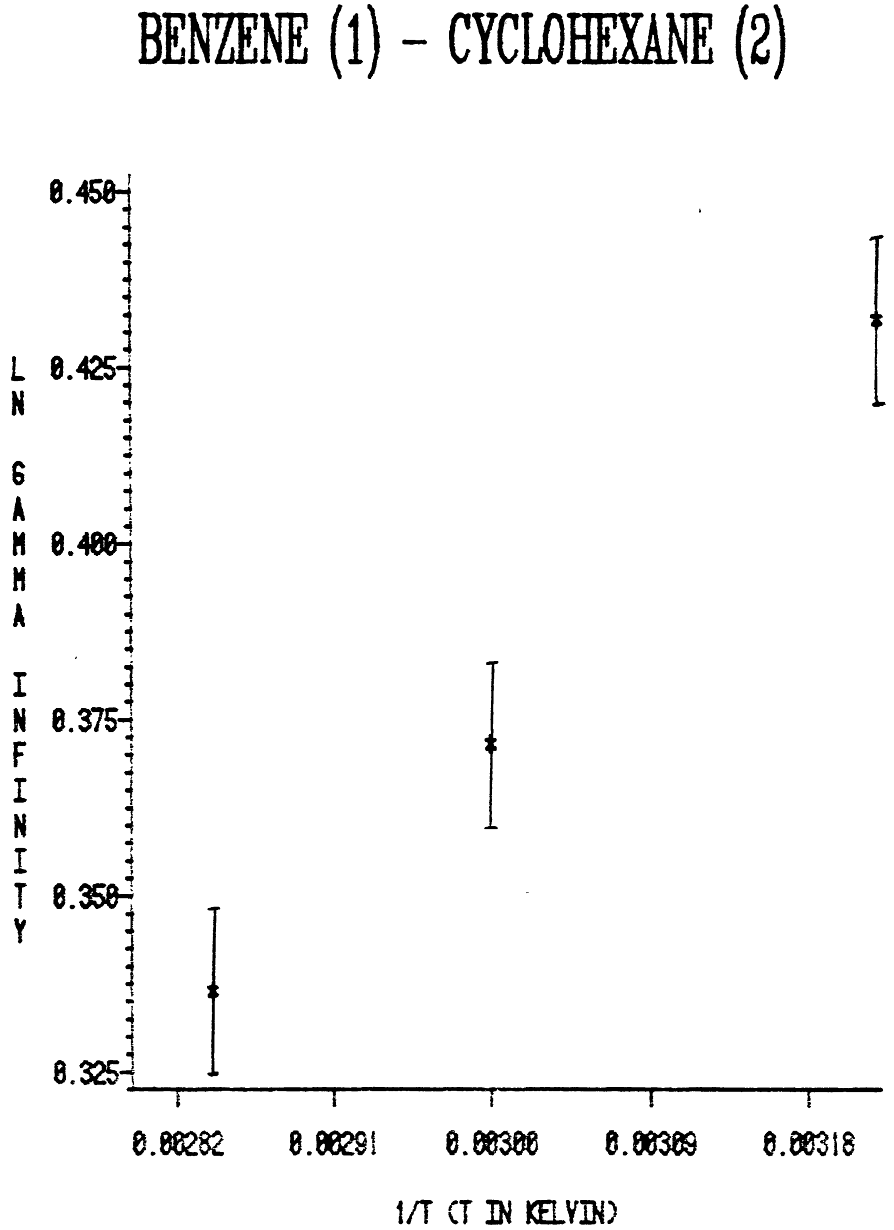


Figure 9. Infinite Dilution Activity Coefficient for Benzene in Cyclohexane

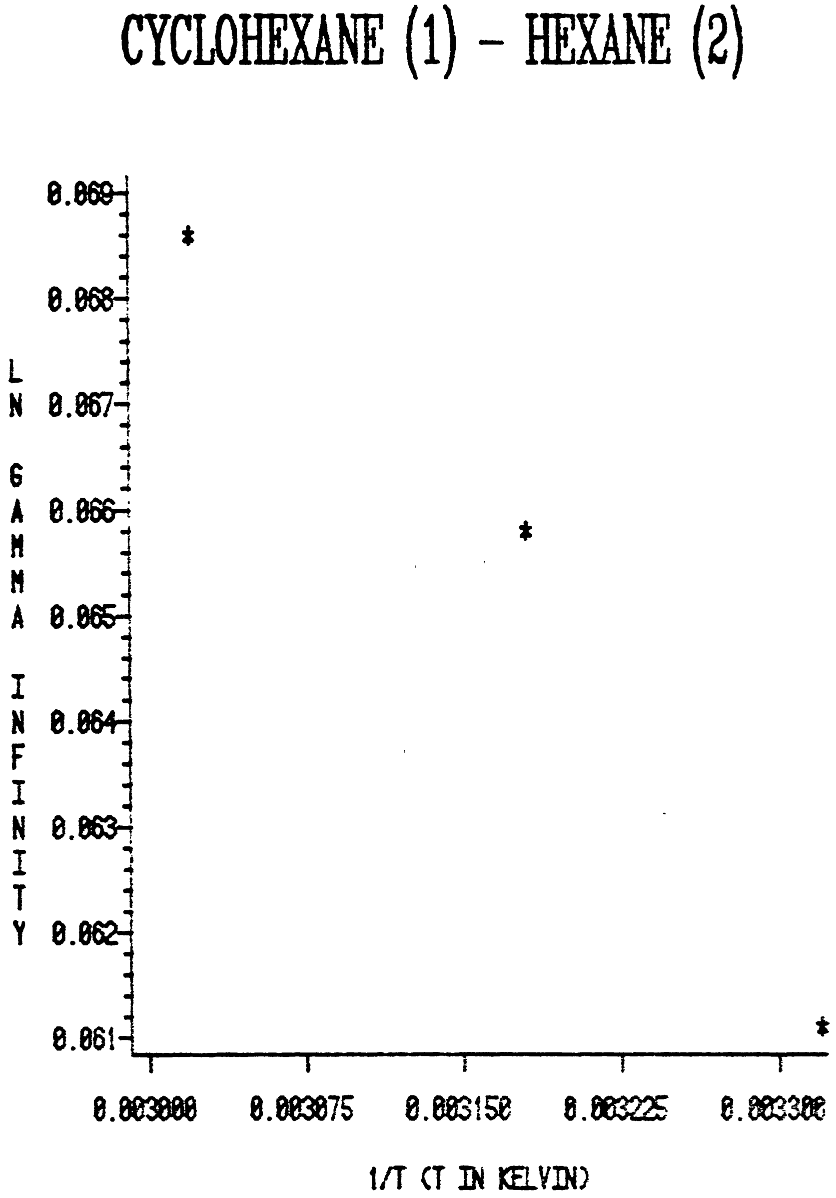


Figure 10. Infinite Dilution Activity Coefficient for Cyclohexane in Hexane

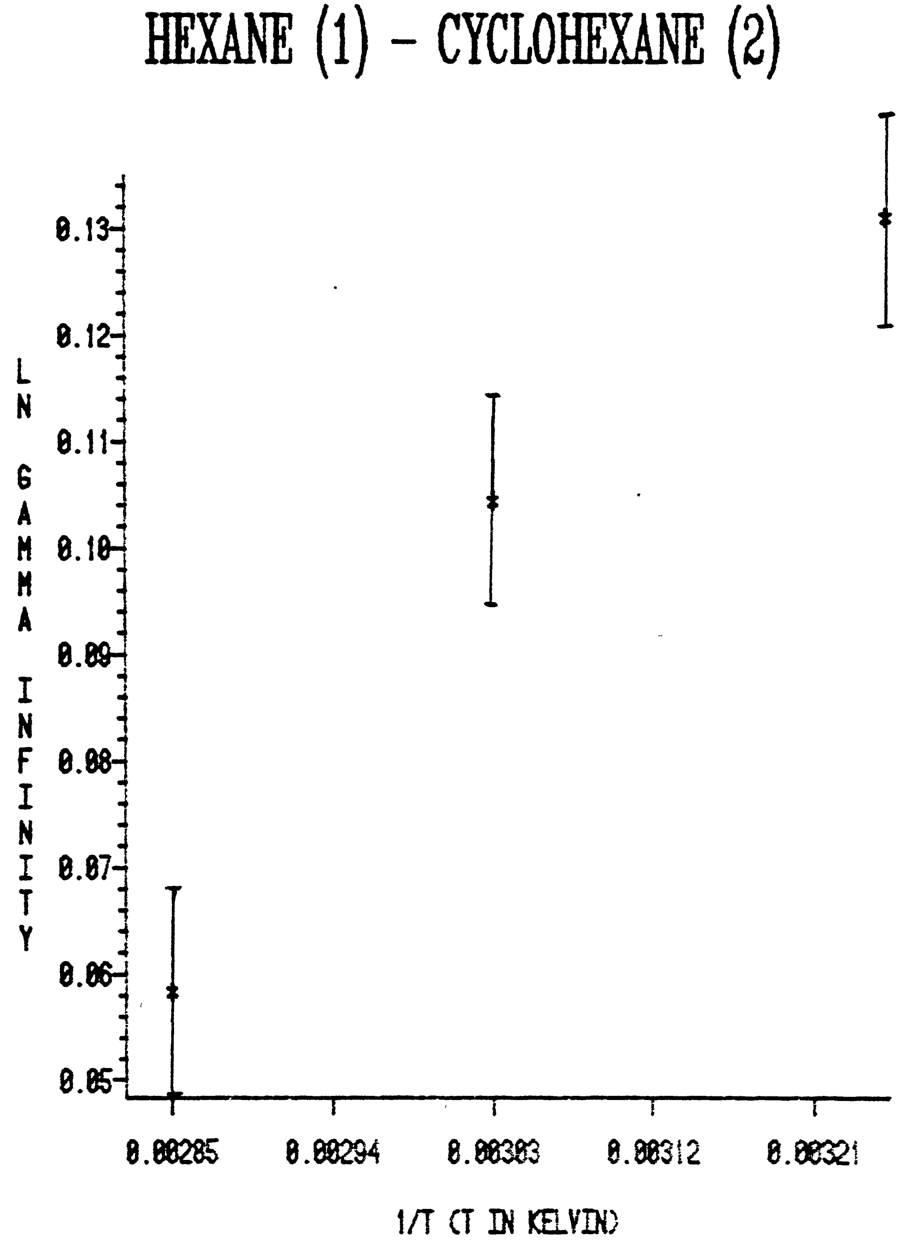


Figure 11. Infinite Dilution Activity Coefficient for Hexane in Cyclohexane

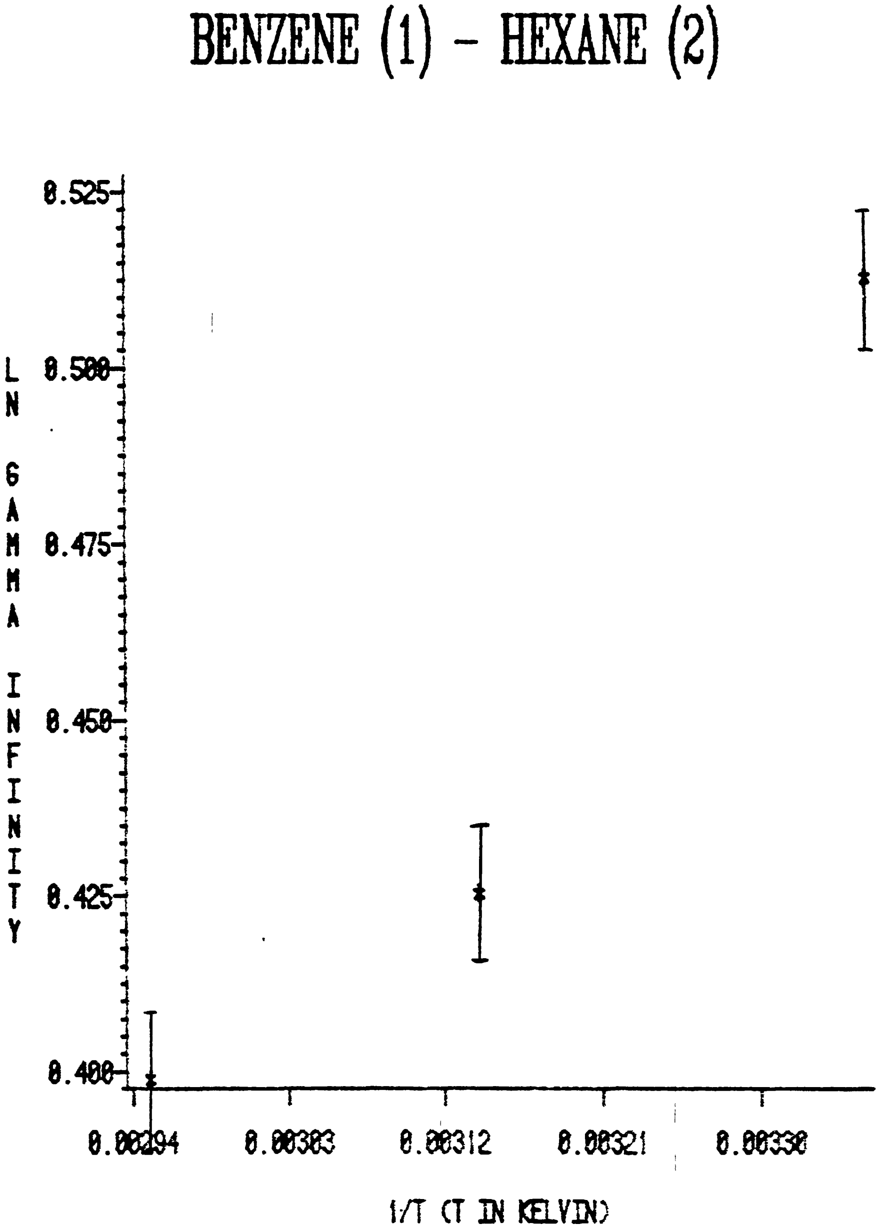


Figure 12. Infinite Dilution Activity Coefficient for Benzene in Hexane

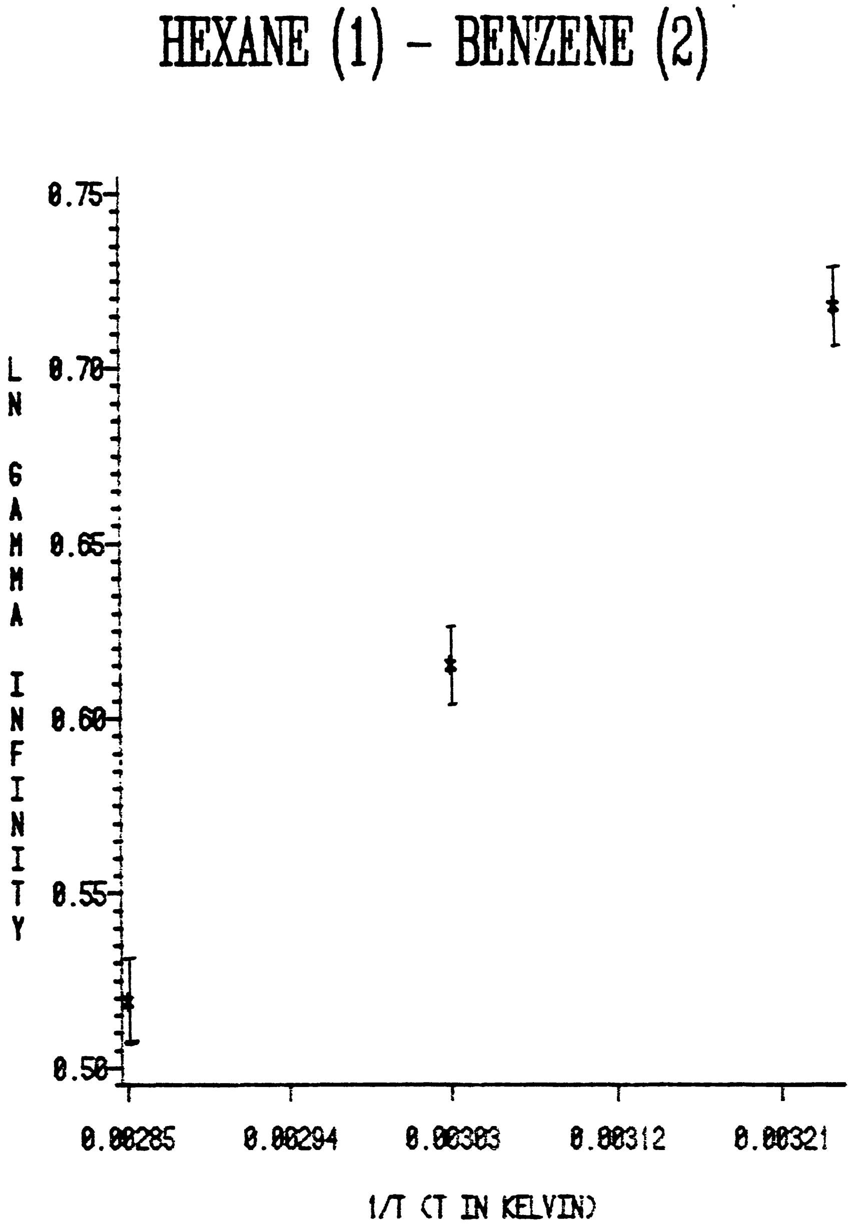


Figure 13. Infinite Dilution Activity Coefficient for Hexane in Benzene

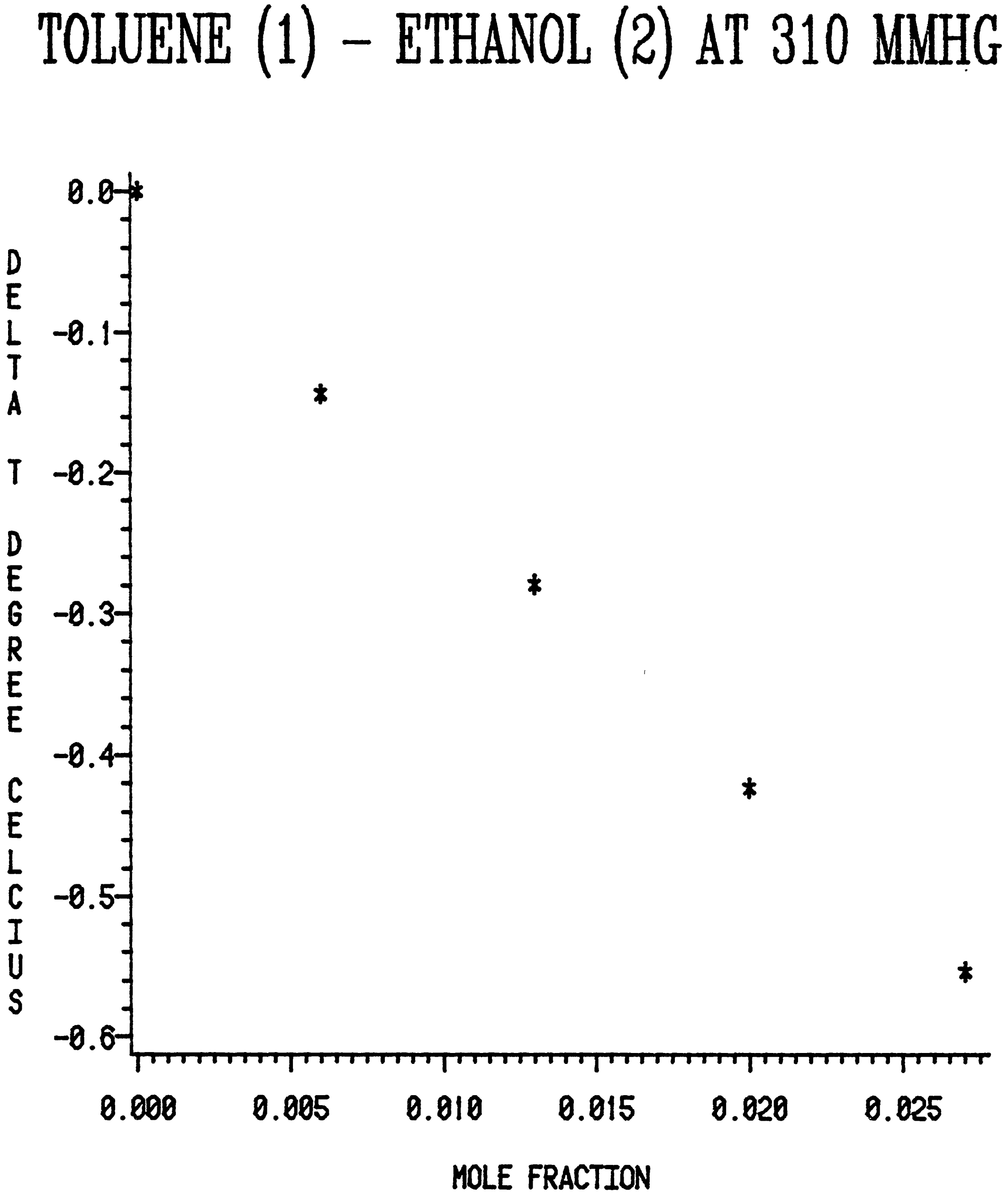


Figure 14. Effect of Composition on the Boiling Point Temperature of the Binary System Toluene (1) - Ethanol (2)

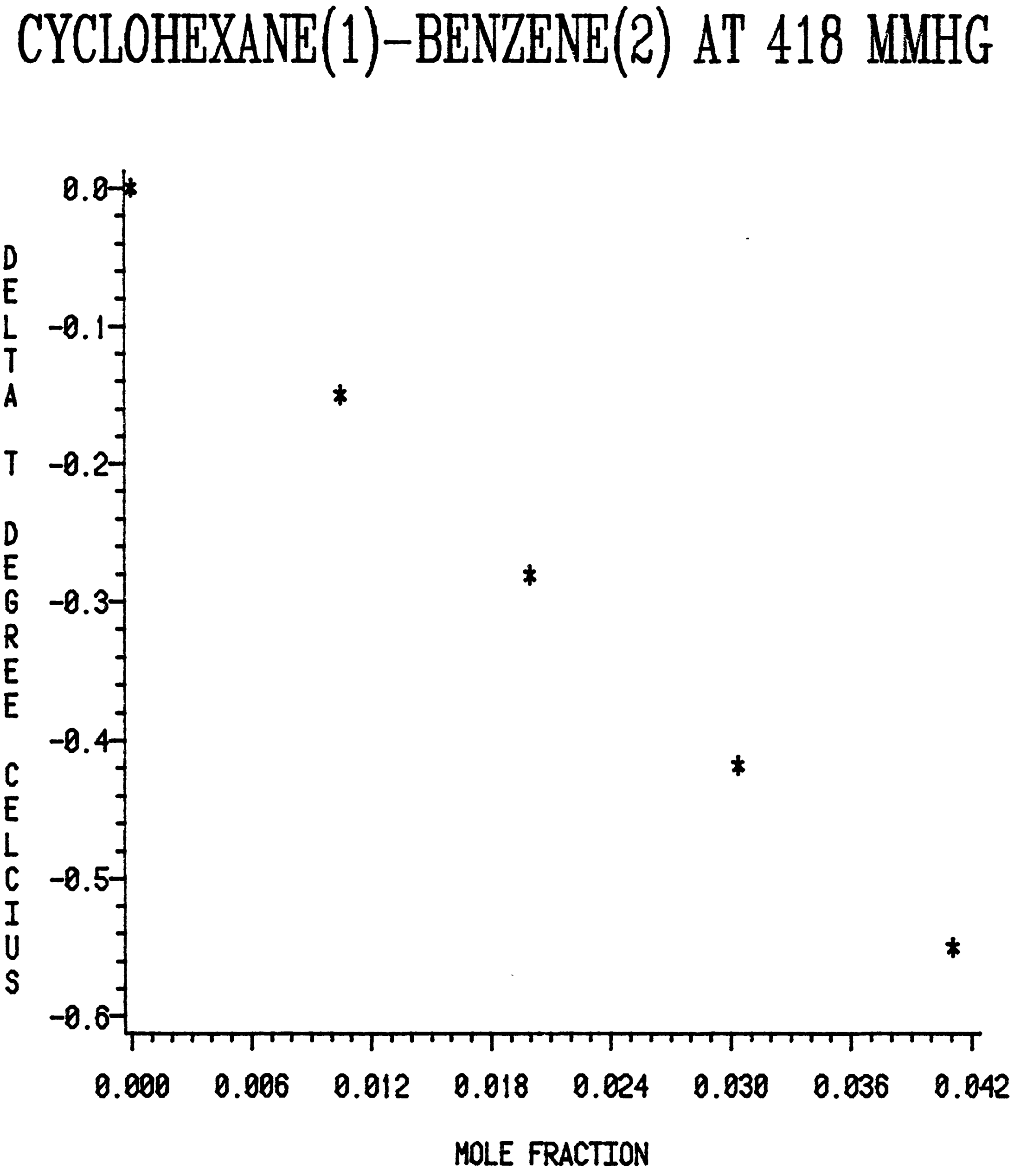


Figure 15. Effect of Composition on the Boiling Point Temperature of the Binary System Cyclohexane (1) - Benzene (2)

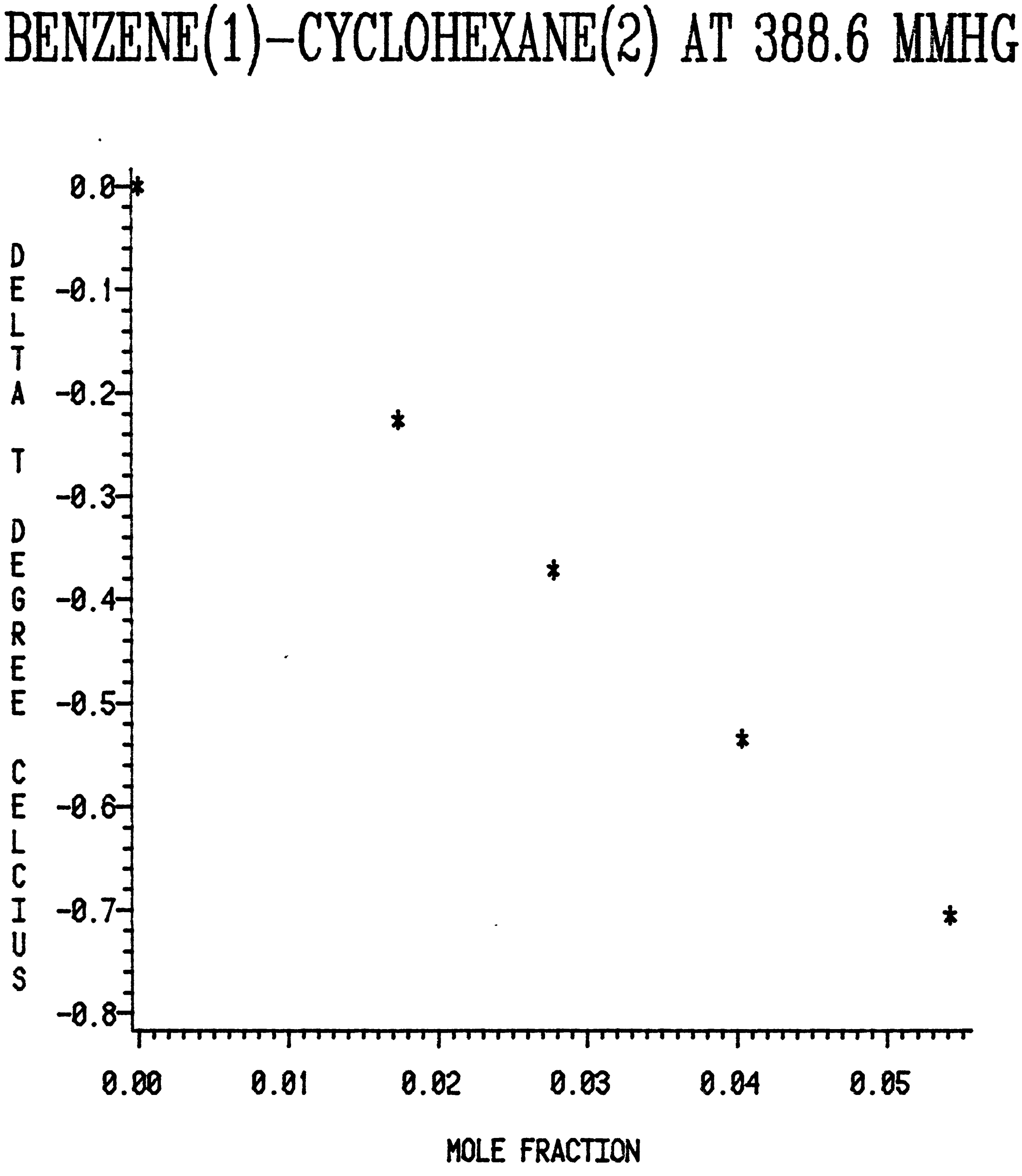


Figure 16. Effect of Composition on the Boiling Point Temperature of the Binary System Benzene (1) - Cyclohexane (2)

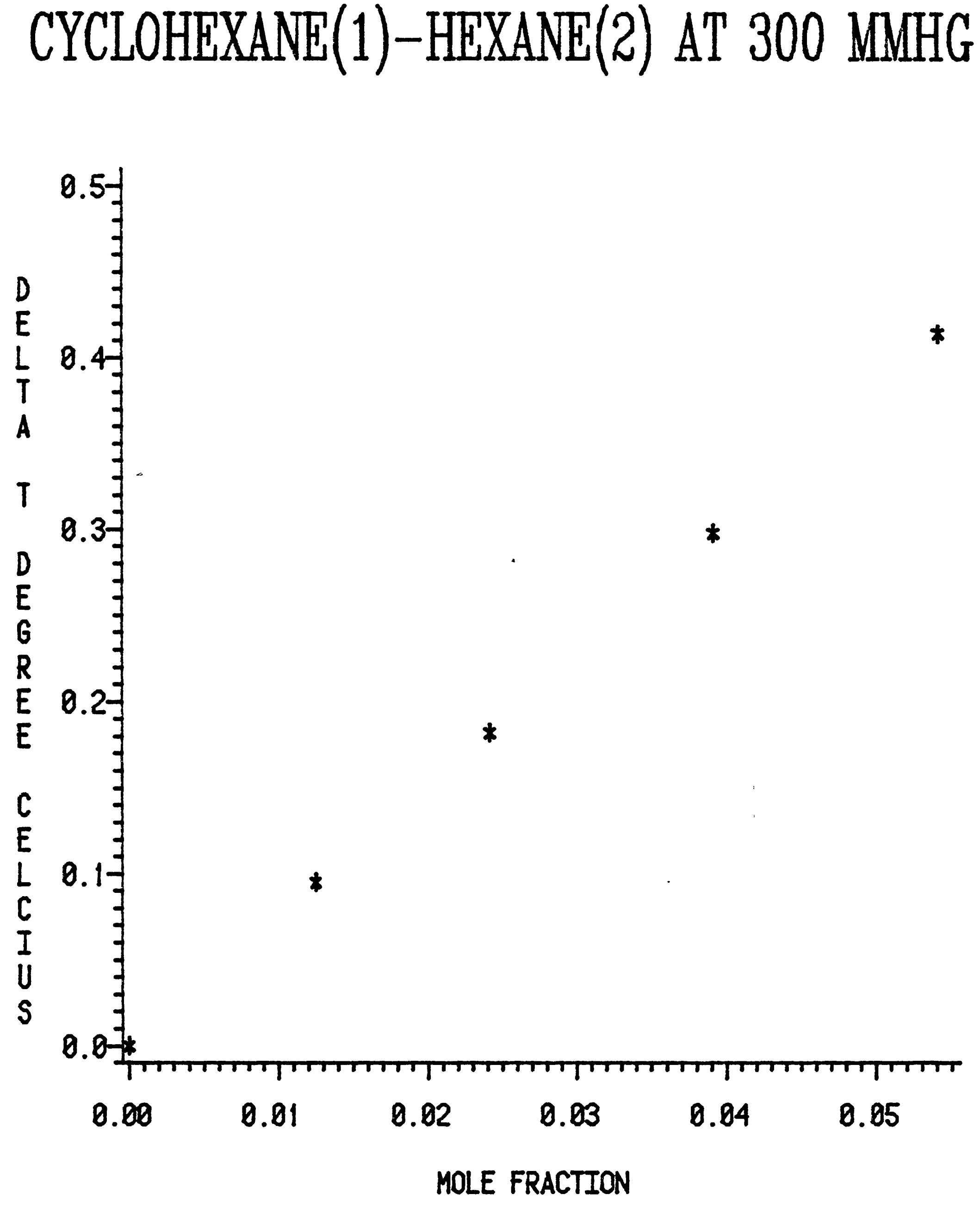


Figure 17. Effect of Composition on the Boiling Point Temperature of the Binary System Cyclohexane (1) - Hexane (2)

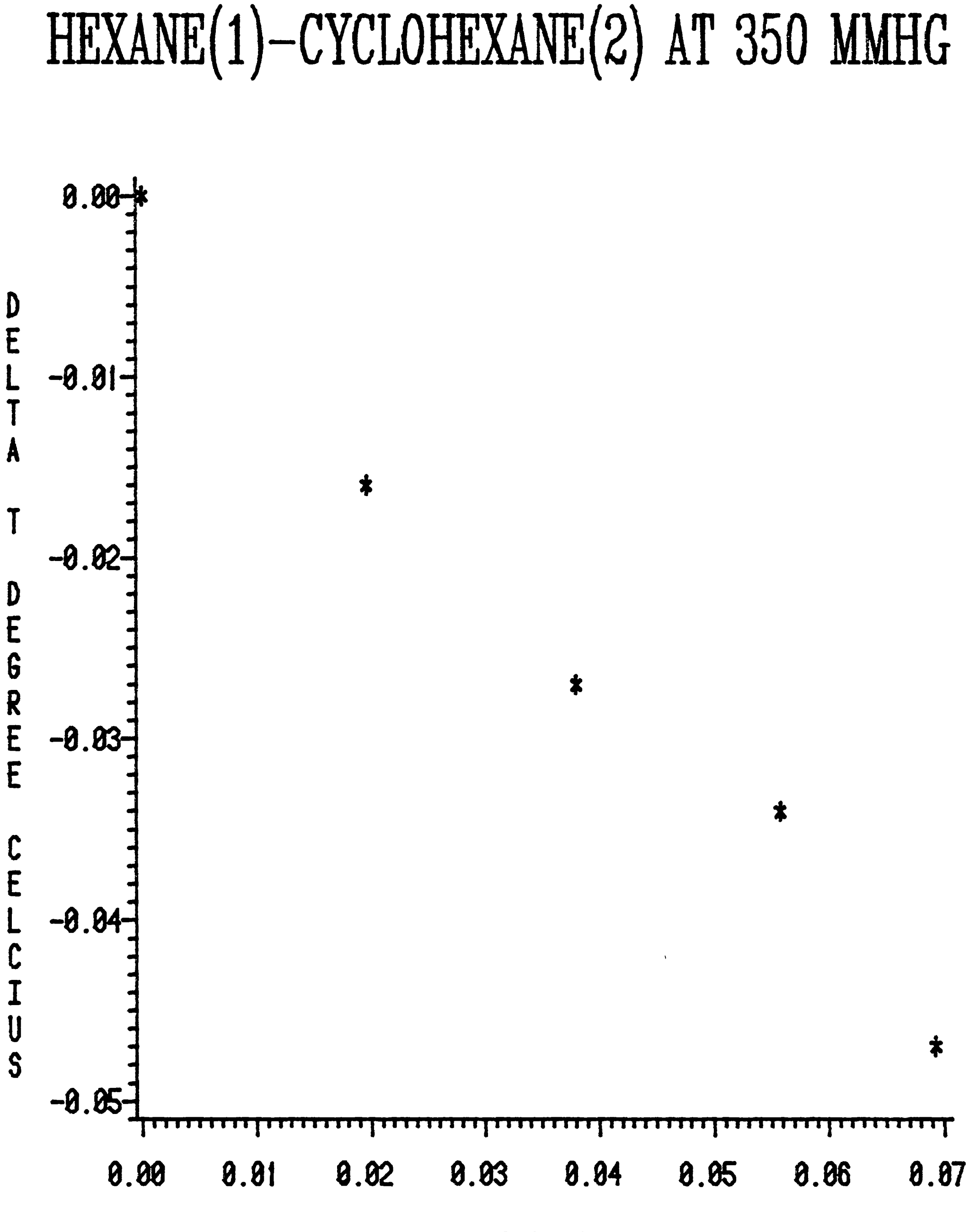


Figure 18. Effect of Composition on the Boiling Point Temperature of the Binary System Hexane (1) - Cyclohexane (2)

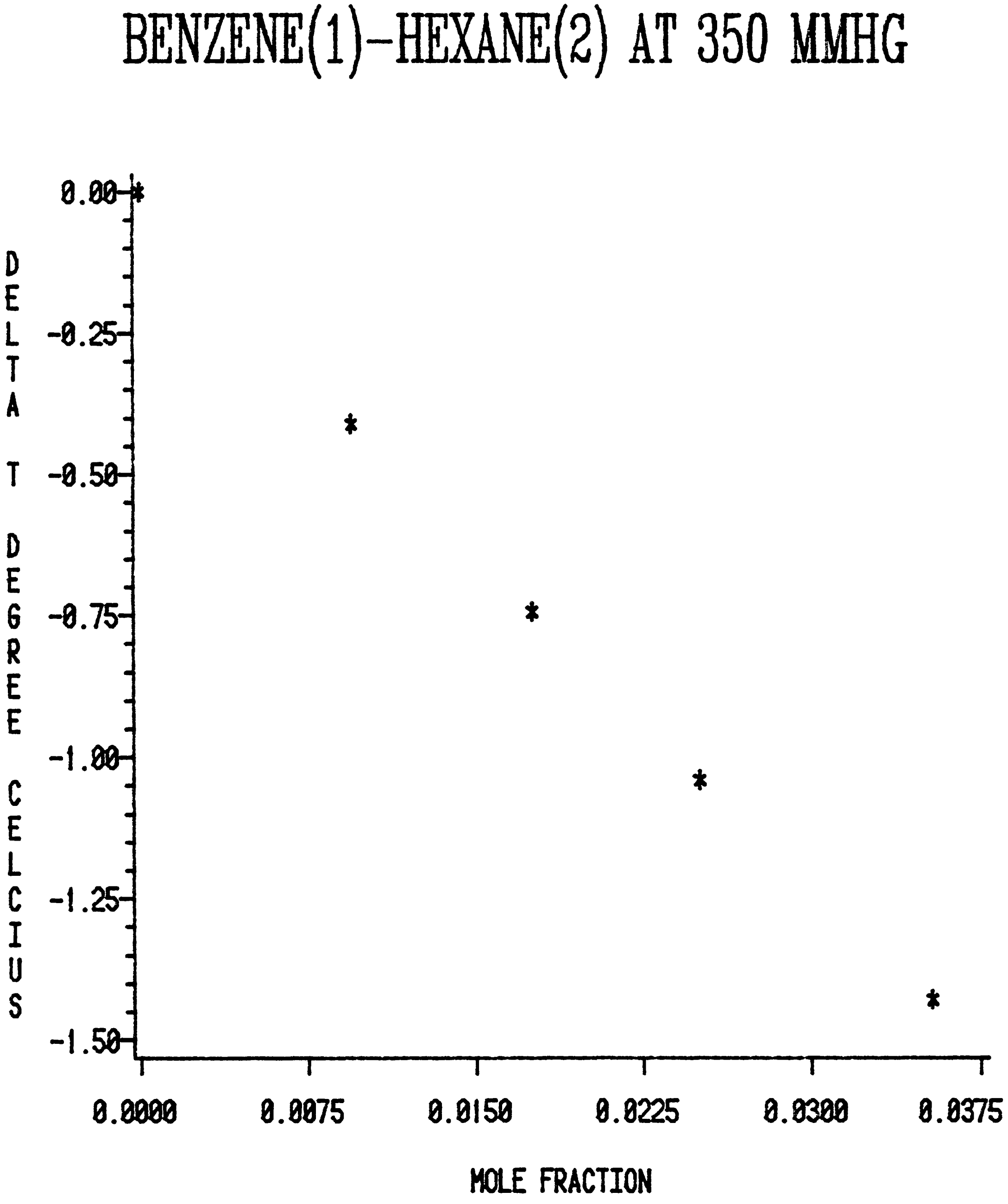


Figure 19. Effect of Composition on the Boiling Point Temperature of the Binary System Benzene (1) - Hexane (2)

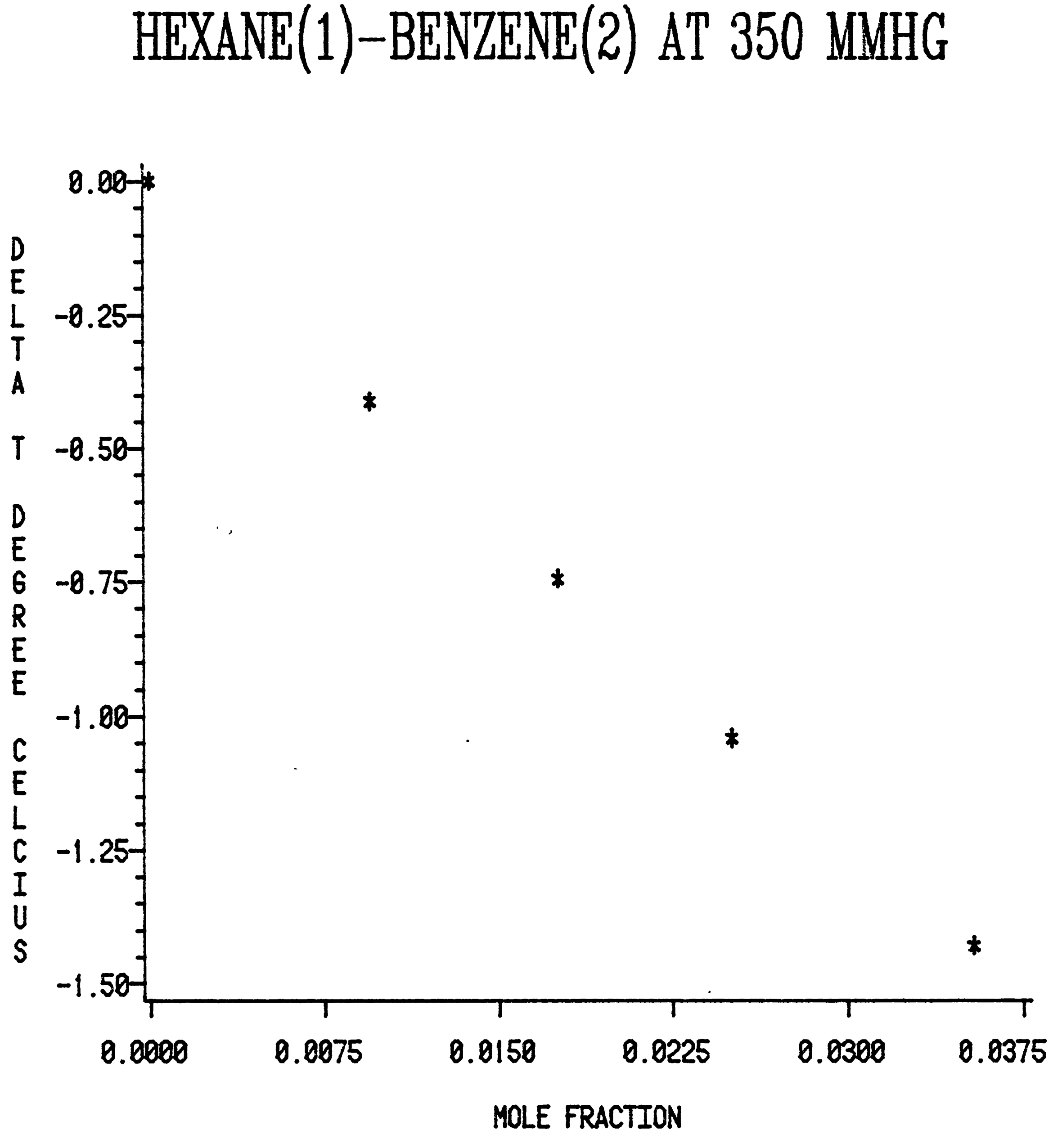


Figure 20. Effect of Composition on the Boiling Point Temperature of the Binary System Hexane (1) - Benzene (2)

composition on boiling point temperature. Again the linearity of the experimental data demonstrates the reliability of the experimental technique. Nearly the same change in the boiling point temperature is observed for a given amount of solute added in all of the binary systems studied. Figure 21 shows infinite dilution activity coefficients for the seven systems studied in this work. This plot is included to show relative magnitudes of γ_1^{∞} for the various systems. The activity coefficients range between 1.06 and 6.23 for a temperature range of 24.950 C to 78.690 C. The largest activity coefficients correspond to the toluene (1) - ethanol (2) system. This means that the above system is a very non-ideal mixture. This can be attributed to the polarity of ethanol through its -OH bond. Ethanol was the only alcohol studied in this work. The hydrocarbons demonstrate similar non-idealities proven by the fact that the activity coefficients for all three groups: paraffins, naphthenes and aromatics are in the range of 1.06 to 2.05. In this range, paraffins and naphthenes exhibit similar non-idealities, while the aromatics are more non-ideal in a given mixture.

Discussion

Differential ebulliometry was used to obtain the data presented in Table VIII. The infinite dilution activity coefficients of all the systems studied are shown in Figure 21. The temperature fluctuations were reduced to about $\pm 5\times10^{-3}$°C by using a magnetic pump to provide forced circulation of the boiling liquid-vapor mixtures. Light hydrocarbons representing normal paraffins, naphthenes, and aromatics were used in this study because these compounds are important in chemical and petroleum processes and, primarily, because data are

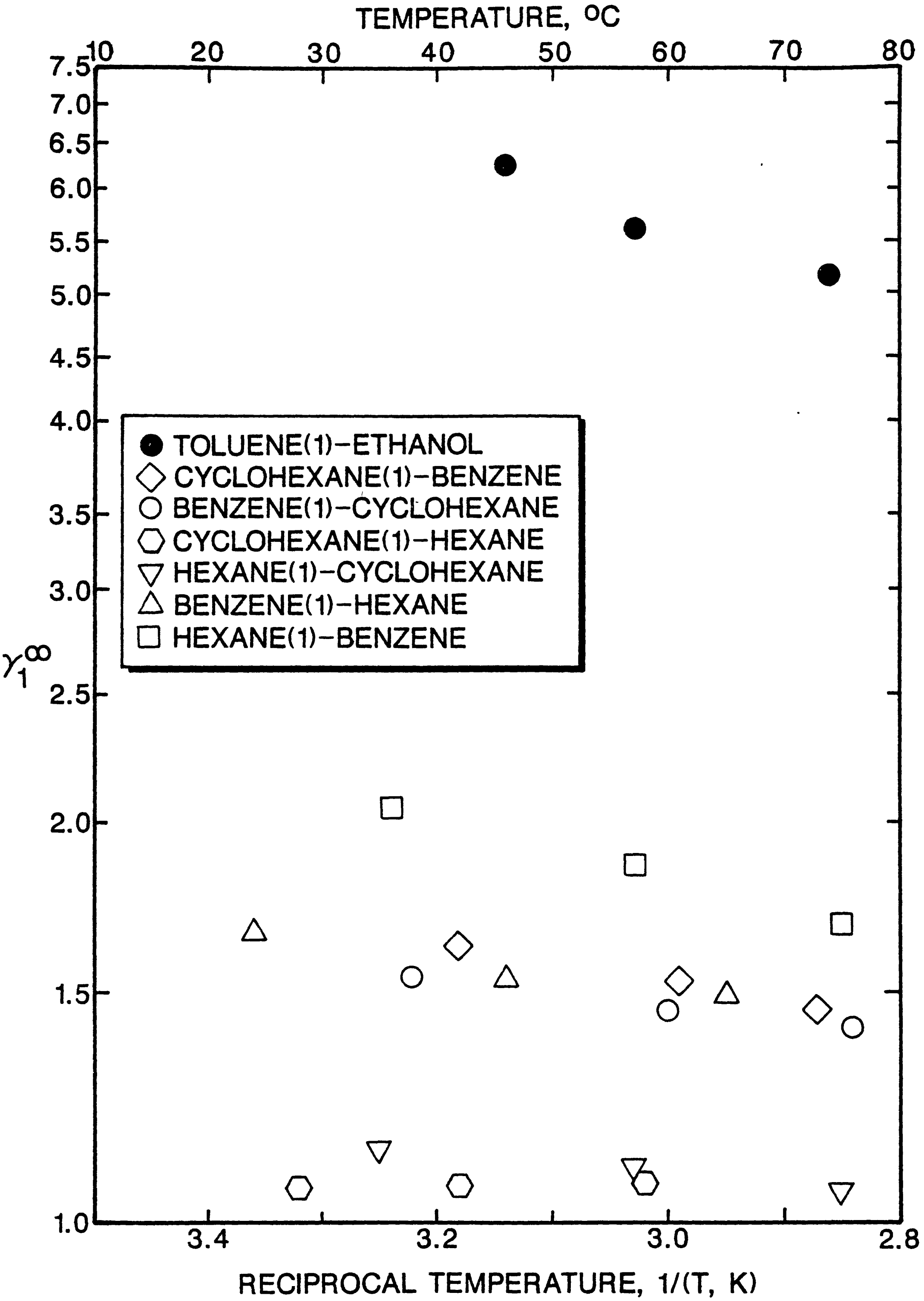


Figure 21. Comparison of Infinite Dilution Activity Coefficients for the Systems Studied

available in the literature for γ_1^∞ values which provide a means to assess the results from the modified ebulliometer.

Of the two models used to fit the data, the quadratic model gave better results, as expected. The differences between the experimental boiling point temperatures and the calculated values were on the order of 0.01 C for the linear case and 0.005 C for the quadratic case. The agreement is well within the experimental accuracy of the data. Since the quadratic model gives results which are more consistent with the experimental uncertainties, there is no reason why this model should not be used exclusively.

Plots of the effect of temperature on γ_1^∞ are a measure of the consistency of data. Figures 22 and 23 show a comparison of the measured γ_1^∞ values with data from the literature. The data of this work, the experimental ebulliometric data of Eckert et al., the data obtained by Kretchmer, Scatchard, and Nagata (30) from the graphical extrapolation of vapor-liquid equilibrium data, and the Wilson and Van Laar fits of the vapor-liquid equilibrium data are all shown in Figures 22 and 23. These figures were taken from reference (30) directly and the experimental data of this work were simply superimposed on Eckert's plot. The line drawn through the data points is based on the data of Eckert only.

Figure 22 shows the case where this work differs most with the Eckert data. The trend of the data points of this work have a different slope than the line based on Eckert's data; however, the other points are also scattered. In Figure 23, much better agreement is observed between the data of this work and those of Eckert et al. This is a more typical representation of the agreement observed between the two

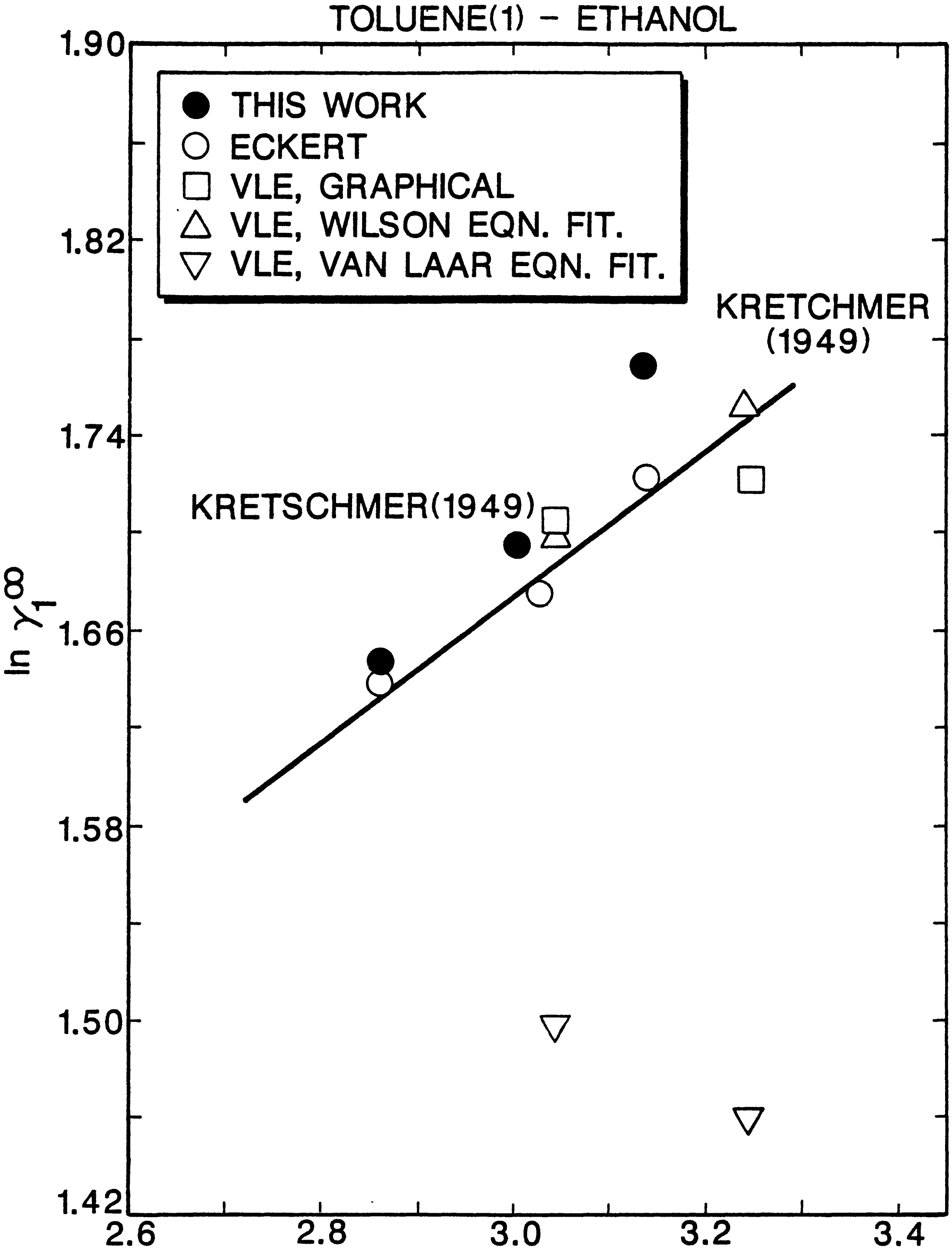


Figure 22. Comparison of Infinite Dilution Activity Coefficients for the Binary System Toluene (1) - Ethanol (2)

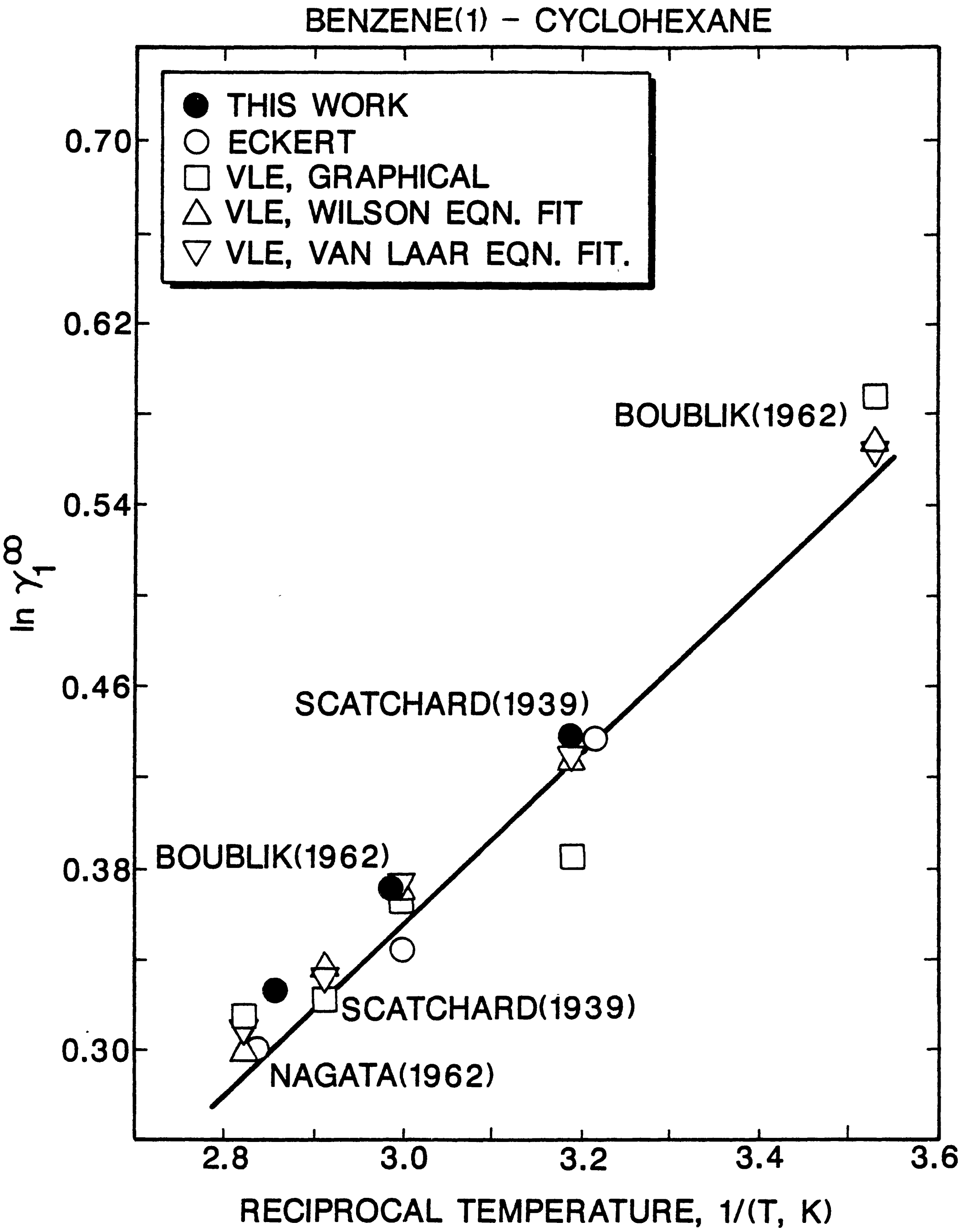


Figure 23. Comparison of Infinite Dilution Activity Coefficients for the Binary System Benzene (1) - Cyclohexane (2)

works. In fact, the present data appear to be in marginally better agreement with other workers' data than do the data of Eckert et al.

The sensitivity of the aquired data to the estimated amount of liquid holdup is illustrated in Table IX. The estimated value of liquid holdup used in the calculations was 2 cc. Results are shown for the systems with the lowest γ_1^∞ (hexane (1)-cyclohexane (2) system), and the highest γ_1^∞ (toluene (1)-ethanol (2) system). Values of 0.2 cc and 5 cc were used to test the sensitivity. As can be seen from this table, the smaller the holdup, the smaller the correction in the liquid mole fraction, which results in a smaller value for the infinite dilution activity coefficient. The effect of the liquid holdup is (as expected) greater on the larger γ_1^∞'s. (The quadratically fitted γ_1^∞ was used in these comparisons.) The five percent change in the values of infinite dilution activity coefficient corresponding to a holdup range of 0.2 cc to 5 cc suggests that the reduced data obtained in this work with an estimate of liquid holdup equal to 2 cc would not be far from the actual values.

An attempt was made to study heavier hydrocarbons such as decane and 1-methylnaphthalene as a test of the performance of the apparatus for such components. When heavy hydrocarbons were used as solutes in light hydrocarbons, the performance of the apparatus was quite satisfactory, but Equation (12) failed to produce reliable results. Eckert (6) argues that when the solute is much less volatile than the solvent, as in the case of decane (1)-hexane (2) studied in this work, the ebulliometric method of determining infinite dilution activity coefficients may not be applicable. This was proven to be the case in the decane (1)-hexane (2) system, where a negative value of γ_1^∞ was

TABLE IX

EFFECT OF LIQUID HOLDUP ON CALCUATED INFINITE DILUTION ACTIVITY COEFFICIENTS

Liquid Holdup, cc	Calculated Value of γ_1^{∞} Hexane(1)-Cyclohexane(2)	Toluene(1)-Ethanol(2)
0.2	1.055	6.096
2	1.060	6.226
5	1.067	6.399

obtained using Equation (12). There is a 105°C difference between the boiling points of hexane and decane, and this could explain the failure of Equation (12) and the ebulliometric technique.

When heavy hydrocarbons were used as both solute and solvent, e.g., decane (1)-1-methylnaphthalene (2), the performance of the apparatus was not satisfactory. The higher temperatures at which the heavier hydrocarbons boiled resulted in the flaking off of the fused crushed glass inside the annulus section of the ebulliometer. This glass found its way into the magnetic pump and stopped its operation. The thick-walled tygon tubing was also attacked by the high boiling chemicals (specially aromatics) and collapsed.

Since the infinite dilution activity coefficient was calculated in an iterative manner, a one constant Margules Equation was deemed sufficient. Additional constants would not have much effect on the final γ_1^∞ values, but they would have made the calculations more difficult.

The linear and quadratic statistical fits gave infinite dilution activity coefficients which differed from one another by at most 6%, as shown in Table VIII.

The operating pressure in this work ranged between 150.0 mmHg and 726.7 mmHg. Typical values of the low, medium, and high pressures at which the experiments were conducted were 150 mmHg, 350 mmHg, and 700 mmHg. The above pressures corresponded to boiling point temperatures between 24.95°C to 78.69°C.

The first objective of this work which was to build and test a modified ebulliometer for better operation at low pressures was accomplished successfully. However, the second objective of this work which was to study heavy solvent-solute pairs was not achieved due mainly to mechanical problems such as the plugging of the magnetic vane-type pump with flaked off crushed glass, and the collapse of tygon tubing at the high temperatures at which heavier hydrocarbons such as normal decane and 1-methylnaphthalene boiled.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The compact ebulliometer (which requires only about 110 cc of solvent) designed by Eckert and coworkers (6) was modified in this work to replace the thermosiphon-dependent circulation in the ebulliometer by a forced convection operation. This modification enhanced appreciably the performance of the ebulliometer at low pressures by improving the boiling behavior as a result of the constant flow of boiling liquid and vapor provided to the glass spiral on the thermometer well.

The system was tested using light hydrocarbons, and the performance was quite satisfactory. The data obtained were compared to those of other investigators (Table VIII, Figures 22 and 23) and were shown to be in good agreement (maximum deviation of 5%).

The performance of the apparatus was unsatisfactory when heavy hydrocarbons were used. The ebulliometric technique was shown not to be suitable for mixtures with widely varying boiling points (high relative volatility), as expected from the analysis given by Eckert et al. (6).

Recommendations

The apparatus of this work demonstrated excellent performance at low pressures with light hydrocarbons and should continue to be used. A few minor modifications could render it suitable for heavy hydrocarbons, as well. The recommended modifications follow.

1. A more powerful magnetic pump could be used to reduce temperature fluctuations at high temperatures (greater than 150°C) by providing a higher flow rate of the boiling mixture to the thermometer well.
2. Installation of a mesh screen at the pump inlet would eliminate the possibility of the flaked-off crushed glass entering the pump and stopping its operation.
3. Use of Teflon tubing which is less sensitive to the attack of high-boiling aromatics could prevent the problems caused by the failure of the tygon tubing.

The quartz thermometer can operate at temperatures to 250°C. An attempt should be made to test heavier chemicals (which have boiling points below 250°C) in the apparatus once the above modifications have been implemented. A glass vacuum jacket should be used at high temperatures to avoid heat loss to the surroundings.

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APPENDIXES

APPENDIX A

COMPUTER PROGRAM FOR DATA REDUCTION

The following program was developed to reduce the experimental data to yield infinite dilution activity coefficients. It calculates a Margules Constant (Equation (29)) using the overall uncorrected mole fractions ($x = z$) based on a linear and a quadratic model:

$$\Delta T = ax \qquad \text{(linear)} \qquad (31)$$

$$\Delta T = ax + bx^2 \qquad \text{(quadratic)} \qquad (32)$$

It then uses the Margules constant to make corrections for the vapor and liquid holdups using molar material balances (Equations (38), (39)). Once the corrected values of the mole fractions are known, the program uses the same linear and quadratic functions to calculate "a" in the above equations and consequently the infinite dilution activity coefficient (Equation (12)).

```
C     THIS PROGRAM MAKES CORRECTIONS FOR THE VAPOR AND LIQUID
C     HOLD-UPS BASED ON LINEAR AND QUADRATIC MODELS OF DELTA T VS X
C     AND THEN CALCULATES THE INFINITE DILUTION ACTIVITY COEFFICIENT
      REAL MW1,MW2,P1,P2,M2,M20,Y1(10),Y2(10)
      REAL K1(10),K2(10),M1(10),M(10),T(10),VLG(10),ROLG(10)
      DIMENSION X(10),Y(10),Z(10),ZC(10),T1(10)
      DIMENSION XC(10),XT(10),X2(10),AZ(10),AM1(10)
      DIMENSION ROL(10),ROV(10),VL(10),VV(10)
      DIMENSION TCALC(10),DELTAT(10),X2T(10),X3(10),X4(10)
      WRITE (6,79)
79    FORMAT (1H1,/////,'      SYSTEM: TOLUENE(1)-ETHANOL(2)')
      READ (9,*) N,P,R,TC,P3,AM20
C     N IS THE NUMBER OF INJECTIONS
C     P IS THE SYSTEM PRESSURE IN PSIA
C     R IS THE GAS CONSTANT
C     TC IS THE BOILING POINT OF PURE SOLVENT IN DEGREES C
C     P3 IS THE VAPOR PRESSURE OF THE SOLUTE IN PSIA
C     AM20 IS THE GRAMS OF SOLVENT CHARGED
      WRITE (6,*) '     VALUES OF N,P,R'
      WRITE (6,*) N,P,R
      WRITE (6,*) '     VALUES OF TC,P3,AM20'
      WRITE (6,*) TC,P3,AM20
      WRITE (6,*) '     VALUES OF T(1) THROUGH T(N)'
      DO 1001 L=1,N
      READ (9,*) T1(L)
C     T(1) THROUGH T(N) ARE THE EXPERIMENTAL DELTA T IN DEGREE C
      WRITE (6,*) T1(L)
1001  CONTINUE
      WRITE (6,*) '     VALUES OF AM1(1) THROUGH AM1(N)'
      DO 1002 L=1,N
      READ (9,*) AM1(L)
C     AM1(1) THROUGH AM1(N) ARE THE GRAMS OF SOLUTE INJECTED
      WRITE (6,*) AM1(L)
1002  CONTINUE
      WRITE (6,*) '     VALUES OF PC1,PC2,TC1,TC2'
      READ (9,*) PC1,PC2,TC1,TC2
C     PC1 IS THE CRITICAL PRESSURE OF COMPONENT 1 IN PSIA
C     PC2 IS THE CRITICAL PRESSURE OF COMPONENT 2 IN PSIA
C     TC1 IS THE CRITICAL TEMPERATURE OF COMPONENT 1 IN K
C     TC2 IS THE CRITICAL TEMPERATURE OF COMPONENT 2 IN K
      WRITE (6,*) PC1,PC2,TC1,TC2
      WRITE (6,*) '     VALUES OF VVY,VLY,VX,VZ'
      READ (9,*) VVY,VLY,VX,VZ
C     VVY IS THE VAPOR VOLUME IN THE EBULLIOMETER IN CC
C     VLY IS THE CONDENSED VAPOR VOLUME IN CC
C     VX IS THE LIQUID VOLUME IN CC
C     VZ IS THE INITIAL VOLUME IN CC
      WRITE (6,*) VVY,VLY,VX,VZ
```

```
      WRITE (6,*) '     VALUES OF A11,A21,A31'
      READ (9,*) A11,A21,A31
C     A11,A21,AND A31 ARE ANTOINE CONSTANTS OF COMPONENT 1
      WRITE (6,*) A11,A21,A31
      WRITE (6,*) '     VALUES OF A12,A22,A32'
      READ (9,*) A12,A22,A32
C     A12,A22,AND A32 ARE THE ANTOINE CONSTANTS OF COMPONENT 2
      WRITE (6,*) A12,A22,A32
      WRITE (6,*) '     VALUES OF AR1,AR2,MW1,MW2'
      READ (9,*) AR1,AR2,MW1,MW2
C     AR1 AND AR2 ARE RACKETT EQUATION CONSTANTS
C     MW1 AND MW2 ARE THE MOLECULAR WEIGHTS OF SOLUTE AND SOLVENT
      WRITE (6,*) AR1,AR2,MW1,MW2
      LQ=1
      TK=TC+273.15
C     TK IS THE BOILING POINT TEMPERATURE OF THE SOLVENT IN KELVIN
      TF=TC*1.8+32
C     TF IS THE BOILING POINT TEMPERATURE OF THE SOLVENT IN DEGREE F
      M2O=AM2O/MW2
C     GRAMS OF SOLVENT CONVERTED TO MOLES OF SOLVENT
      DO 112 I=1,N
      M1(I)=AM1(I)/MW1
C     GRAMS OF SOLUTE CONVERTED TO MOLES OF SOLUTE  .
      Z(I)=M1(I)/(M1(I)+M2O)
C     MOLES OF SOLUTE ARE CONVERTED TO MOLE FRACTION
112   CONTINUE
      DO 123 I=1,N
      X(I)=Z(I)
      AZ(I)=Z(I)
C     THE LIQUID MOLE FRACTION IS SET EQUAL TO THE INITIAL VALUE
123   CONTINUE
      Q=1
      GO TO 134
8     Q=1
41    DO 16 I=1,N
1     DO 977 K=1,N
      T(K)=T1(K)
977   CONTINUE
      P1=PC1*EXP(A11-(A21/(A31+TF+(T(I)*1.8))))
C     P1 IS THE VAPOR PRESSURE OF THE SOLUTE CALCULATED BY ANTOINE EQ
      P2=PC2*EXP(A12-(A22/(A32+TF+(T(I)*1.8))))
C    P2 IS THE VAPOR PRESSURE OF THE SOLVENT CALCULATED BY ANTOINE EQ
      J=0
      X(I)=Z(I)
      VL1=83.147*TC1*(14.696/PC1)*AR1**(1+(1-((TK+T(I))/TC1))**0.2857
     +1)
      VL2=83.147*TC2*(14.696/PC2)*AR2**(1+(1-((TK+T(I))/TC2))**0.2857
     +1)
```

```
C     HERE THE LIQUID MOLAR VOLUMES OF COMPONENTS 1 AND 2 ARE
C     CALCULATED USING THE RACKETT EQUATION
15    VL(I)=VL1*X(I)+VL2*(1-X(I))
C     THIS IS THE MIXTURE MOLAR VOLUME IN CC/GMOL
      J=J+1
      ROL(I)=1/VL(I)
C     ROL IS THE LIQUID DENSITY IN GMOL/CC
57    K1(I)=(P1/P)*EXP(A*(1-X(I))**2)
      K2(I)=(P2/P)*EXP(A*X(I)**2)
C     THESE ARE THE EQUILIBRIUM CONSTANTS OF COMPONENTS 1 & 2
      Y1(I)=K1(I)*X(I)
      Y2(I)=K2(I)*(1-X(I))
C     THESE ARE THE VAPOR MOLE FRACTIONS
      Y(I)=Y1(I)/(Y1(I)+Y2(I))
C     Y IS NORMALIZED HERE
      VLG(I)=VL1*Y(I)+VL2*(1-Y(I))
      ROLG(I)=1/VLG(I)
C     VLG AND ROLG ARE THE CONDENSED VAPOR MOLAR VOLUME AND DENSITY
      ROV(I)=P/(R*(TK+T(I))*14.696)
101   M(I)=M1(I)-((VVY*ROV(I)+VLY*ROLG(I))*Y(I))
      M2=M20-((VVY*ROV(I)+VLY*ROLG(I))*(1-Y(I)))
C     THESE ARE THE COMPONENT MOLE BALANCES
      XC(I)=M(I)/(M(I)+M2)
C     THIS IS THE NEW VALUE OF X USING THE MATERIAL BALANCE
      IF (ABS(XC(I)-X(I)).LE.0.0001) GO TO 16
C     THIS IS THE CONVERGENCE CRITERION
      X(I)=XC(I)
      GO TO 15
16    CONTINUE
      IF (LQ.EQ.2) GO TO 1340
C     ******************************************************************
C     THIS SECTION IS USED IF A LINEAR FIT IS DESIRED
134   DO 154 I=1,N
      XT(I)=X(I)*T1(I)
      X2(I)=X(I)**2
154   CONTINUE
      DO 19 I=2,N
      XT(I)=XT(I)+XT(I-1)
      X2(I)=X2(I)+X2(I-1)
C     THESE ARE SUMMATIONS USED TO GET THE DT/DX TERM
19    CONTINUE
      DT=XT(N)/X2(N)
C     THIS IS THE DT/DX TERM
      DO 185 I=1,N
      TCALC(I)=DT*X(I)
C     THIS IS THE LINEARLY FITTED VALUE OF DELTA T
      DELTAT(I)=T1(I)-TCALC(I)
C     THIS IS THE DIFFERENCE BETWEEN THE EXPERIMENTAL AND THE
C     STATISTICALLY OBTAINED DELTA T
```

```
      DP2=P*(A22/((TF+A32)**2))
C     THIS IS THE DP2/DT TERM
      G1=(P-(DP2*DT*1.8))/P3
C     THIS THE INFINITE DILUTION ACTIVITY COEFFICIENT
      IF (Q.EQ.2) GO TO 43
      AG1=G1
      WRITE (6,79)
      WRITE (6,998)
998   FORMAT (///,2X,'     LINEAR MODEL:')
      WRITE (6,731) AG1
731   FORMAT (///,'       THE ORIGINAL VALUE OF G1 IS: ',F10.5)
      Q=Q+1
      A=ALOG(G1)
C     THIS IS THE MARGULES CONSTANT
      GO TO 41
43    AC=ALOG(G1)
      IF (ABS(AC-A).LE.0.001) GO TO 420
      A=AC
      DO 146 J=1,N
      XT(J)=0
      X2(J)=0
146   CONTINUE
      GO TO 41
420   WRITE (6,1840)
1840  FORMAT (///,6X,'INJECTION NO',6X,'Z(I)',10X,'X(I)',10X,'T(I)',
     +8X,'TCALC(I)',8X,'DELTAT(I)')
      WRITE (6,1860) I,Z(I),X(I),T1(I),TCALC(I),DELTAT(I)
1860  FORMAT (12X,I5,2X,5(F12.5,2X))
185   CONTINUE
      GO TO 1000
C     ****************************************************************
C     THIS SECTION IS USED IF A QUADRATIC FIT IS DESIRED
1340  DO 1440 I=1,N
      XT(I)=X(I)*T1(I)
      X2(I)=X(I)**2
      X3(I)=X(I)**3
      X4(I)=X(I)**4
      X2T(I)=X2(I)*T1(I)
1440  CONTINUE
      DO 190 I=2,N
      XT(I)=XT(I)+XT(I-1)
      X2(I)=X2(I)+X2(I-1)
      X3(I)=X3(I)+X3(I-1)
      X4(I)=X4(I)+X4(I-1)
      X2T(I)=X2T(I)+X2T(I-1)
C     THESE ARE SUMMATIONS USED TO GET THE DT/DX TERM
190   CONTINUE
      B=(XT(N)-(X2T(N)*X2(N))/X3(N))/(X3(N)
     +-(X4(N)*X2(N)/X3(N)))
```

```
C         THIS IS THE COEFFICIENT OF X**2 IN THE QUADRATIC FIT
          DT=(XT(N)-B*X3(N))/X2(N)
C         THIS IS THE DT/DX TERM
          DO 1850 I=1,N
          TCALC(I)=DT*X(I)+B*(X(I)**2)
C         THIS IS THE CALCULATED VALUE OF T
          DELTAT(I)=T1(I)-TCALC(I)
C         THIS IS THE DIFFERENCE BETWEEN THE EXPERIMENTAL AND THE
C         STATISTICALLY FIT VALUE OF DELTA T
          DP2=P*(A22/((TF+A32)**2))
C         THIS IS THE DP2/DT TERM
          G1=(P-(DP2*DT*1.8))/P3
C         THIS IS THE INFINITE DILUTION ACTIVITY COEFFICIENT
          IF (Q.GE.2) GO TO 430
          AG1=G1
          WRITE (6,79)
          WRITE (6,999)
999       FORMAT (///,2X,'     QUADRATIC MODEL:')
          WRITE (6,737) G1
737       FORMAT (///,'       THE ORIGINAL VALUE OF G1 IS: ',F10.5)
          Q=Q+1
          A=ALOG(G1)
C         THIS IS THE MARGULES CONSTANT
          GO TO 41
430       AC=ALOG(G1)
          IF (ABS(AC-A).LE.0.001) GO TO 42
          A=AC
          DO 1980 J=1,N
          XT(J)=0
          X2(J)=0
          X3(J)=0
          X4(J)=0
          X2T(J)=0
1980      CONTINUE
          GO TO 41
42        WRITE (6,184)
184       FORMAT (///,6X,'INJECTION NO',6X,'Z(I)',10X,'X(I)',10X,'T(I)',
     +    8X,'TCALC(I)',8X,'DELTAT(I)')
          WRITE (6,186) I,Z(I),X(I),T1(I),TCALC(I),DELTAT(I)
186       FORMAT (12X,I5,2X,5(F12.5,2X))
1850      CONTINUE
C ******************************************************************
1000      WRITE (6,23)
23        FORMAT('0',5X,'TC',12X,'P',11X,'G1',10X,'DT',10X,'DP2',12X,'A')
          WRITE (6,20) TC,P,G1,DT,DP2,A
```

```

20        FORMAT (4X,6(F10.5,2X))
          EP=((G1-AG1)/G1)*100
          WRITE (6,937) EP
937       FORMAT (///,2X,'     THE PERCENT CHANGE IN G1 IS: ',F10.5)
          IF (LQ.EQ.2) GO TO 657
          LQ=LQ+1
          GO TO 8
657       STOP
          END
```

```
SYSTEM: TOLUENE(1)-ETHANOL(2)
VALUES OF N,P,R
      5            3.4820000           82.0500000
VALUES OF TC,P3,AM20
     45.6000000            1.4829990           84.3314900
VALUES OF T(1) THROUGH T(N)
     -0.2250000
     -0.4060000
     -0.5910000
     -0.7220000
     -0.8800000
VALUES OF AM1(1) THROUGH AM1(N)
      1.3267000
      2.5341990
      3.8789990
      4.9127990
      6.2798000
VALUES OF PC1,PC2,TC1,TC2
    587.8000000          925.3000000          591.7900000          516.2600000
VALUES OF VVY,VLY,VX,VZ
    200.0000000            2.0000000            2.0000000          106.0000000
VALUES OF A11,A21,A31
      5.9442500         5836.2850000          374.7451000
VALUES OF A12,A22,A32
      7.4358190         6162.3590000          359.3825000
VALUES OF AR1,AR2,MW1,MW2
      0.2646000            0.2520000           92.1139900           46.0690000
```

```
SYSTEM: TOLUENE(1)-ETHANOL(2)


 LINEAR MODEL:


 THE ORIGINAL VALUE OF G1 IS:     5.30019


INJECTION NO        Z(I)            X(I)            T(I)          TCALC(I)          DELTAT(I)
          1         0.00781         0.00763        -0.22500        -0.19745        -0.02755


INJECTION NO        Z(I)            X(I)            T(I)          TCALC(I)          DELTAT(I)
          2         0.01481         0.01450        -0.40600        -0.37512        -0.03088


INJECTION NO        Z(I)            X(I)            T(I)          TCALC(I)          DELTAT(I)
          3         0.02249         0.02206        -0.59100        -0.57065        -0.02035


INJECTION NO        Z(I)            X(I)            T(I)          TCALC(I)          DELTAT(I)
          4         0.02831         0.02780        -0.72200        -0.71926        -0.00274


INJECTION NO        Z(I)            X(I)            T(I)          TCALC(I)          DELTAT(I)
          5         0.03591         0.03531        -0.88000        -0.91350         0.03350
TC             P             G1          DT           DP2            A
45.60001     3.48200      5.35352   -25.86975     0.09572       1.67758


 THE PERCENT CHANGE IN G1 IS:     0.99625
```

```
SYSTEM: TOLUENE(1)-ETHANOL(2)


 QUADRATIC MODEL:


 THE ORIGINAL VALUE OF G1 IS:    5.85281


INJECTION NO       Z(I)          X(I)          T(I)         TCALC(I)        DELTAT(I)
          1        0.00781       0.00760      -0.22500       -0.22150      -0.00350


INJECTION NO       Z(I)          X(I)          T(I)         TCALC(I)        DELTAT(I)
          2        0.01481       0.01445      -0.40600       -0.40598      -0.00002


INJECTION NO       Z(I)          X(I)          T(I)         TCALC(I)        DELTAT(I)
          3        0.02249       0.02199      -0.59100       -0.59270       0.00170


INJECTION NO       Z(I)          X(I)          T(I)         TCALC(I)        DELTAT(I)
          4        0.02831       0.02772      -0.72200       -0.72318       0.00118


INJECTION NO       Z(I)          X(I)          T(I)         TCALC(I)        DELTAT(I)
          5        0.03591       0.03521      -0.88000       -0.87877      -0.00123
TC             P            G1         DT          DP2           A
45.60001     3.48200     5.86640   -30.28419    0.09572     1.76919


 THE PERCENT CHANGE IN G1 IS:    0.23169
```

APPENDIX B

DERIVATION OF γ_1^∞ EXPRESSION

The criterion for equilibrium between two phases "I" and "II" is that their chemical potentials be equal:

$$\mu_i^I = \mu_i^{II} \quad (i = 1,N) \tag{1}$$

if "I" is taken as the vapor phase and "II" is taken as the liquid phase, the vapor-liquid equilibrium is demonstrated by:

$$\mu_i^V = \mu_i^L \tag{2}$$

In a given phase, the quantity μ_i for any component can be expressed as the sum of two terms:

$$\mu_i = \mu_i^0 + \Delta\mu_i \tag{3}$$

The term μ_i^0 is the chemical potential of component "i" in the standard state, where standard state refers to the property of the pure component at the system temperature and total pressure. The quantity $\Delta\mu_i$ is known as the partial molal free energy of mixing and is evaluated in terms of the activity coefficient, γ, as follows.

$$\Delta\mu_i = RT \ln(\gamma_i x_i) \tag{4}$$

Therefore Equation (3) can be rewritten as:

$$\mu_i = \mu_i^0 + RT \ln(\gamma_i x_i) \tag{5}$$

When Equation (5) is applied to two phases (vapor and liquid) in equilibrium, using Equation (2):

$$(\mu_i^0)^V + RT\ \ln(\gamma_i^V x_i^V) = (\mu_i^0)^L + RT\ \ln(\gamma_i^L x_i^L) \tag{6}$$

where $x_i^L = x_i$ is the liquid composition, and $x_i^V = y_i$ is the vapor composition. Upon rearranging:

$$RT\ \ln \frac{x_i \gamma_i^L}{y_i \gamma_i} = (\mu_i^0)^V - (\mu_i^0)^L \tag{7}$$

The equilibrium ratio is defined as:

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i^L}{\gamma_i^V} \exp \left[\frac{(\mu_i^0)^L - (\mu_i^0)^V}{RT}\right] \tag{8}$$

Using the following thermodynamic relationship:

$$d\mu_i = -s_i dT + v_i dP \tag{9}$$

and integrating between the total system pressure and the vapor pressure of component "i", at constant temperature (dT = 0):

$$\Delta\mu_i = \int_{P_i^s}^{P} (v_i)^L\, dP \tag{10}$$

$$\Delta\mu_i = \int_{P_i^s}^{P} \frac{z_i RT}{P}\, dP \tag{11}$$

$$\Delta\mu_i = RT\ \ln \frac{P}{P_i^s} - \int_{P_i^s}^{P} \left[\frac{RT}{P} - (v_i)^V\right] dP \tag{12}$$

$$(\mu_i^0)^V - (\mu_i^0)^L = (v_i)^L (P^s - P) + RT\ \ln \frac{P}{P^s} - \int_{P^s}^{P} \left[\frac{RT}{P} - (v_i)^V\right] dP \tag{13}$$

Substituting in Equation (9):

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i^L}{\gamma_i^V}\,\frac{P_i^s}{P}\exp\left[\frac{(v_i)^L(P - P_i^s)}{RT}\right] \exp \left\{\frac{1}{RT}\int_{P_i^s}^{P} (v_i)^V]\, dP\right\} \tag{14}$$

The fugacity of component "i" is defined as follows:

$$f_i^s = P_i^s \exp\left\{\frac{1}{RT}\int_0^{P_i^s} \left[(v_i)^V - \frac{RT}{P}\right] dP\right\} \tag{15}$$

$$f_i^P = P \exp \left\{\frac{1}{RT}\int_0^{P} \left[(v_i)^V - \frac{RT}{P}\right] dP\right\} \tag{16}$$

$$\frac{f_i^s}{f_i^P} = \frac{P_i^s}{P} \exp \left\{\frac{1}{RT}\int_{P_i^s}^{P} \left[\frac{RT}{P} - (v_i)^V\right] dP\right\} \tag{17}$$

Substituting Equation (17) in Equation (14):

$$\frac{y_i}{x_i} = \frac{\gamma_i^L}{\gamma_i^V}\,\frac{f_i^s}{f_i^P} \exp \left[\frac{(v_i)^L\,(P - P_i^s)}{RT}\right] \tag{18}$$

For a binary system:

$$f_1 P y_1 = \frac{\gamma_1^L}{\gamma_1^V}\, f_1^S\, x_1 \exp\left[\frac{(v_1)^L\,(P - P_1^s)}{RT}\right] \tag{19}$$

$$f_2 P y_2 = \frac{\gamma_2^L}{\gamma_2^V}\, f_2^S\, x_2 \exp\left[\frac{(v_2)^L\,(P - P_2^s)}{RT}\right] \tag{20}$$

Using the definition of the fugacity coefficient:

$$\phi_i = \frac{f_i}{P} = \exp \left\{\frac{1}{RT}\int_0^{P} \left[(v_i)^V - \frac{RT}{P}\right] dP\right\} \tag{21}$$

Equations (19) and (20) can be rewritten as:

$$Py_1\phi_1^P = \frac{\gamma_1^L}{\gamma_1^V} P_1^s\phi_1^s x_1 \exp\left[\frac{(v_1)^L\,(P - P_1^s)}{RT}\right] \tag{22}$$

$$Py_2\,\phi_2^P = \frac{\gamma_2^L}{\gamma_2^V} P_2^s\phi_2^s x_2 \exp\left[\frac{(v_2)^L\,(P - P_2^s)}{RT}\right] \tag{23}$$

For a binary system:

$$P = P(y_1 + y_2) \tag{24}$$

Solving Equation (22) and (23) for Py_1 and Py_2 and adding:

$$P = \frac{\gamma_1^L\phi_1^s}{\gamma_1^V\phi_1^P} P_1^s x_1 \exp\left[\frac{(v_1)^L(P-P_1^s)}{RT}\right] + \frac{\gamma_2^L\phi_2^s}{\gamma_2^V\phi_2^P} P_2^s x_2 \exp\left[\frac{(v_2)^L(P-P_2^s)}{RT}\right] \tag{25}$$

Assuming ideal gas phase solution: $\gamma_1^V = \gamma_2^V = 1$, and differentiating with respect to solute composition:

$$\frac{dP}{dx_1} = P_1^s\phi_1^s \exp\left[\frac{(v_1)^L(P-P_1^s)}{RT}\right]\left[\frac{\gamma_1 x_1 (v_1)^L}{\phi_1^P RT}\frac{dP}{dx_1} - \frac{\gamma_1 x_1}{(\phi_1^P)^2}\frac{d\phi_1^P}{dP}\frac{dP}{dx_1} + \right.$$

$$\left.\frac{x_1}{\phi_1^P}\frac{d\gamma_1}{dx_1} + \frac{\gamma_1}{\phi_1^P}\right] + P_2^s\phi_2^s \exp\left[\frac{(v_2)^L(P-P_2^s)}{RT}\right]\left\{\frac{\gamma_2 x_2 (v_2)^L}{\phi_2^P\,RT}\frac{dP}{dx_2} - \right.$$

$$\left.\frac{\gamma_2 x_2}{(\phi_2^P)^2}\frac{d\phi_2^P}{dP}\frac{dP}{dx_2} + \frac{x_2}{\phi_2^P}\frac{d\gamma_2}{dx_2} + \frac{\gamma_2}{\phi_2^P}\right]\frac{dx_2}{dx_1} \tag{26}$$

where the superscripts of γ_1^L and γ_2^L were dropped. Letting x_1 approach zero (infinitely dilute solution):

$$\frac{dx_2}{dx_1} = -1$$

$$\frac{d\gamma_1}{dx_1} = \text{finite at } x_1 = 0$$

$$\gamma_2 \rightarrow 1$$

$$x_2 \rightarrow 1$$

$$\frac{d\gamma_2}{dx_2} \rightarrow 0$$

$$P \rightarrow P_2^S$$

$$\left(\frac{dP}{dx_1}\right)^{\infty} = \frac{\gamma_1^{\infty} P_1^S \phi_1^S}{\phi^{(P_2^S)}} \exp\left[\frac{(v_1)^L (P_2^S - P_1^S)}{RT}\right] + P_2^S \left\{\left[\frac{(v_2)^L}{RT} - \frac{1}{\phi_2^S} \frac{d\phi_2^P}{dP}\right]\left(\frac{d\phi_2^P}{dP}\right)^{\infty} - 1\right\} \tag{27}$$

Solving for γ_1^{∞} :

$$\gamma_1^{\infty} = \frac{\phi_2^S}{(\phi_1^{P_2^S})} \frac{P_2^S\left[1 - \frac{(v_2)^L}{RT} + \frac{1}{\phi_2^S} \frac{d\phi_2^P}{dP} \left(\frac{dP}{dx_1}\right)^{\infty}\right] + \left(\frac{dP}{dx_1}\right)^{\infty}}{P_1^S \exp\left[\frac{(v_1)^L (P_2^S - P_1^S)}{RT}\right]} \tag{28}$$

If the gas phase is ideal gas: $\phi_1 = \phi_2 = 1$ and $\frac{d\phi}{dP} = 0$,

$$\gamma_1^{\infty} = \frac{P_2^S + \left[1 + \frac{P_2^S (v_2)^L}{RT}\right]\left(\frac{dP}{dx_1}\right)_T^{\infty}}{P_1^S} \exp\left[\frac{(v_1)^L (P_1^S - P_2^S)}{RT}\right] \tag{29}$$

If the liquid compressibility factor and the Poynting effect are neglected:

$$\gamma_1^{\infty} = \frac{P_2^S + \left(\frac{dP}{dx_1}\right)_T^{\infty}}{P_1^S} \tag{30}$$

$$\text{but } \left(\frac{dP}{dx_1}\right)_T = -\left(\frac{dP}{dT}\right)_{x_1}\left(\frac{dT}{dx_1}\right)_P \tag{31}$$

and for $x_1 = 0$: $$\left(\frac{dP}{dx_1}\right)_T^{\infty} = -\left(\frac{dP}{dT}\right)\left(\frac{dT}{dx_1}\right)_P^{\infty} \tag{32}$$

$$\gamma_1^{\infty} = \frac{P_2^{s} - \left(\frac{dP_2^{s}}{dT}\right)\left(\frac{dT}{dx_1}\right)_P^{\infty}}{P_1^{s}} \tag{33}$$

APPENDIX C

TABLE OF THE CONSTANTS USED

In the following table all the constants used to obtain and reduce the data are listed. The Antoine Equation constant A_1, and the Rackett Equation constant A are unitless. The units for the other constants are specified in parentheses after the symbol.

Antoine Constants:

Compound	A_1	A_2(°F)	A_3(°F)
Benzene	5.658375	5307.813	379.456
Cyclohexane	5.473055	5030.253	371.2755
Ethanol	7.43437	6162.36	359.3826
Hexane	6.039243	5085.758	382.794
Toluene	5.944251	5836.287	374.745

These constants are consistent with the following Equations:

$$\ln\left(\frac{P_i^0}{P_{ci}}\right) = A_1 - \frac{A_2}{A_3 + T'}$$

where T' is in °F

Critical Properties, Rackett Equation constants, and Molecular Weights

Compound	T_c(K)	P_c(psia)	A	Mol. Wt.
Benzene	562.16	714.2	0.2696	78.12
Cyclohexane	553.54	591.5	0.2729	84.16
Ethanol	516.26	925.3	0.2520	46.07
Hexane	507.43	440.0	0.2635	86.18
Toluene	591.79	587.8	0.2646	92.14

The gas constant: $R = 82.05 \frac{cm^3\ atm}{gmole\ K}$

Values obtained from:

Henley, E.J., Seader, J.D., "Equilibrium Stage Separation Operations in Chemical Engineering", Wiley, New York, 1981, 714-724.

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