PHASE EQUILIBRIA IN
PARTIALLY MISCIBLE SYSTEMS

by 4589

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B.S., National Taiwan University, 1967

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A MASTER'S THESIS

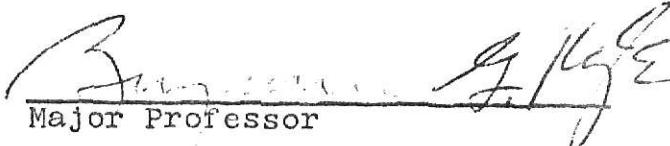submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1970

Approved by:

Major Professor

TABLE OF CONTENTS

I. INTRODUCTION

Precise ternary phase equilibrium data are necessary for the design of separation processes. These data can be obtained from experimental measurements, but this is tedious and expensive. Hence many workers have tried to predict ternary phase behavior from binary information. Prausnitz (1) has convincingly shown that ternary vapor-liquid equilibrium data can be predicted from binary equilibrium data for systems showing small to moderate deviations from ideal solution behavior. He tested several different activity coefficient equations and found that the Wilson equation was superior to other commonly used activity coefficient equations for this prediction. The superior performance of the Wilson equation which contains two parameters per binary system has been recently confirmed by Van Winkle & Holmes (2) who further tested the prediction precedure using addition systems from the literature. Another advantage of the Wilson equation is that the equation for multi-component system contains only binary parameters and will allow the prediction of multi-component equilibrium data using only binary information.

Although the Wilson equation successfully predicts vapor-liquid equilibria, it can not be used for prediction of liquid-liquid equilibria because its algebraic form is such that it is incapable of predicting phase separation. Recently, Renon(3) derived a activity coefficient equation, the NRTL equation,

which contains three parameters per binary system and still has the advantage of the Wilson equation that only binary information in needed. Renon Tested the NRTL equation against literature data and reported it capable of adequately representing activity coefficients, especially in partially miscible systems where large deviations from ideal solution behavior occur.

Joy and Kyle[4] summarized previous attempts to predict ternary liquid-liquid equilibrium data and obtained two conclusions. First, liquid-liquid equilibria for type II ternary systems may be predicted reasonably well when parameters for the two partially miscible binaries are evaluated from mutual solubility data and the completely miscible binary is assumed to behave ideally. Second, reasonable predictions of liquid-liquid equilibria for type I ternary systems can not be expected when the ordinary two-parameter activity coefficient equations are used if parameters for the partially miscible binary were evaluated from mutual solubility data. Joy and Kyle explained these observations by means of an error analysis which showed that the location of the predicted binodal curve is more sensitive to parameter estimation errors for a type I system than for a type II system. A more general explanation for the difficulties encountered in the prediction is that partially miscible systems exhibit extreme deviations from ideal behavior and thus require activity ciefficient equations with more flexibility than the common two-parameter variety. Unfortunately, only two parameters can be evaluated when the mutual solubility data are the only

available data.

Thus it seems desirable to attempt the prediction of type I systems where sufficient binary data are available to allow the use of a three-parameter activity coefficient equation. This study was undertaken to provide the necessary equilibrium data for testing the feasibility of predicting ternary liquid-liquid equilibrium from binary equilibrium data.

Thermodynamics in Fluid-Phase Equilibria

As the criteria of equilibrium are expressed in terms of intensive properties, the conditions under which a vapor-liquid system is in a state of internal equilibrium are that the temperature, pressure, and the fugacity of each component are uniform throughout the whole system. The uniformity of temperature and pressure in the system implys that the system is under thermal and mechanical equilibrium. The fugacity represents the escaping tendency from one phase to another. When the escaping tendency of each component in all phase is the same, the system is in equilibrium. In studying phase equilibria we are most interested in relating the compositions of phases in equilibrium and therefore we need to know how to express fugacities as a functions of temperature, pressure and phase composition.

Fugacity in Gas Mixtures: The fugacity of a component i in the vapor phase, f_i^V, is related to its mole fraction in the vapor phase, y_i, and to the total pressure, P, by introducing a fugacity coefficient

$$f_i^V = \Phi_i \, P \, y_i \tag{1}$$

where the fugacity coefficient, Φ_i, is a function of temperature, total pressure, and composition of the vapor phase. The fugacity coefficient can be expressed as a function of temperature, pressure, and gas phase composition in a rigorous thermodynamic manner via an equation of state if the P-V-T behavior of all the constituents of the mixture are available[5]. Pransnitz and Coworkers[6] have developed methods for calculating the fugacity coefficient which require very little experimental data and yet yield reasonable values. For a perfect gas mixture the fugacity coefficient is unity. Generally, for real gases at moderate pressures the fugacity coefficient will not deviate from unity by more than 10%.

Fugacity in Liquid Mixtures: The liquid-phase fugacity, f_i^L, of component i can be related to its mole fraction in the liquid phase and to a standard-state fugacity, f_i^{OL}, by introducing an activity coefficient, γ_i.

$$f_i^L = \gamma_i \, x_i \, f_i^{OL} \tag{2}$$

The standard-state fugacity, f_i^{OL}, is chosen at the same temperature as the solution, at some fixed composition, and at some specified pressure. For condensable components, the activity coefficient is normalized such that

$$\lim_{x_i \to 1} \gamma_i = 1 \tag{3}$$

In this case, the standard-state fugacity for component i is the fugacity of the pure liquid. At moderate pressures the vapor phase deviation is negligible and the standard-state fugacity of a component can be replaced by its vapor pressure without serious error. Thus equation (2) becomes

$$f_i^L = \gamma_i \, x_i \, P_i^S \tag{4}$$

For a specified system at constant temperature and pressure, the activity coefficient of a component in a liquid phase is a function of the composition in that phase. Several kinds of equations have been proposed for the activity coefficient γ; some have a theoretical basis and some are empirical. There are usually two or three parameters in each equation, which depend on the particular system and which must be determined from experimental data.

Vapor-Liquid Equilibrium: At constant temperature and pressure, the condition of equilibrium can be stated as

$$f_i^V = f_i^L \tag{5}$$

Substituting equation (1) and (2) into equation (5), we obtain

$$\Phi_i \, y_i \, P = x_i \, f_i^{OL} \, \gamma_i \tag{6}$$

In most cases the vapor phase deviation is negligible compared with the liquid phase deviation and without serious error equation (6) can be written

$$y_i \; P = x_i \; P_i^S \; \gamma_i \tag{7}$$

where P_i^S is the saturation vapor pressure of pure liquid i at
temperature T. Equation (7) relates equilibrium vapor phase
composition to its equilibrium liquid phase composition at a
specified temperature and constant pressure. If the activity
coefficient equation and its parameters are known, activity
coefficients can be calculated at specified liquid phase
compositions and thus the vapor phase compositions can be
calculated from Equation (7).

Liquid-Liquid Equilibrium: At constant pressure and temperature,
the condition of equilibrium for a liquid-liquid system is

$$f_i^{L'} \; = \; f_i^{L''} \tag{8}$$

Substituting equation (4) into above equation, we obtain

$$x_i' \; P_i' \; x_i' \; = \; x_i'' \; P_i'' \; x_i'' \tag{9}$$

Because $P_i' = P_i''$, Equation (9) reduces to

$$x_i' \; \gamma_i' \; = \; x_i'' \; \gamma_i'' \tag{10}$$

where x_i' and x_i'' are the mole fractions of component i in each
of the liquid phases and γ_i' and γ_i'' are the corresponding activity
coefficients. If an activity coefficient equation is selected
and its parameters are known, the equilibrium data for a liquid-

liquid system can be predicted by means of equation (10).

Graphical Expression for Ternary Systems

Compositions in a ternary system can be represented graphically by an equilateral triangle. The apexes of the triangle represent pure components A, B, and C. Any point on the edge of the triangle represents a binary mixture of the two components marked at the ends of the edge. The lengths of the perpendiculars from any point within the triangle to the A-B, A-C, and B-C edges represent the concentrations of components C, B, and A respectively.

Figure 1-a shows that a mixture at D when added to component C forms a mixture F which lies on the straight line DFC. The location of F can be determined by the lever arm principle which is basically a mass balance relation. This principle states that

$$\frac{\text{Moles of D}}{\text{Moles of C}} = \frac{\text{the length of FC}}{\text{the length of DF}}$$

if compositions are expressed in mole fractions. Or

$$\frac{\text{Mass of D}}{\text{Mass of C}} = \frac{\text{the length of FC}}{\text{the length of DF}}$$

if compositions are expressed in mass fractions.

Phase equilibrium data for a ternary partially miscible system can be shown conveniently on a triangular diagram. On Figure 1-b a binodal curve, or solubility curve, divides the

diagram into two different solubility regions. Any mixture which has an over-all composition lying within the region enveloped by the binodal curve separates into two coexisting liquid phases. The area outside the binodal curve represents compositions where only one liquid phase exists. A ternary system consisting of one partially miscible binary is called a type I system as shown by Figure 1-b. Ternary systems consisting of two partially miscible binaries are shown on Figures 1-c and 1-d. The system with one continuous two-liquid phase region, Figure 1-d, is more important for engineering design and is refered to as a Type II system. The compositions of two liquid phases in equilibrium are represented by tie lines such as the lines FH on Figure 2. Thus a mixture prepared by mixing components A, B, and C so as to yield an overall composition indicated by M will exist as two liquid phases of compositions F_1 and H_1 at equilibrium . As seen from Figure 2 the tie lines become shorter as the concentration of component A increases. Finally the plait point P at which these two conjugate phases become identical and constitute a single phase is reached. Thus the plait point connects the two separate solubility curves which comprise the binodal curve. Curve DP represents the composition of the equilibrium phase which is rich in component B, and curve PE represents the composition of the other coexisting equilibrium phase which is rich in component C.

Solvent Selectivity

Consider a solution of components 1 and 2 which is to be separated by adding a third component 3 which is miscible with component 1 and partially miscible with component 2. The phase relationship is shown on Figure 3. This figure shows that as a quantity of component 3 is added to the solution which has a original composition M, the composition of the resulting mixture shifts from M to S. Since the mixture S is located within the partially miscible region, the solution separates into two coexisting phases R and T. After the solvent, 3, is extracted from each phase, the composition of each phase reduces to E and D. On figure 3 we see that phase E is richer in component 1 and phase D is richer in component 2, and it is obvious that the most effective separation occurs when the distance between D and E is large.

The solvent selectivity, β_{12}, provides a good measure of the ability of the solvent, component 3, to separate a mixture of component 1 and component 2 and is defined as

$$\beta_{12} = x_1' \, x_2'' \, / \, x_1'' \, x_2' \tag{11}$$

where x_1', x_2' are the mole fractions of component 1 and 2 in the phase which is rich in component 3, and x_1'', x_2'' are the mole fractions of component 1 and 2 in the other liquid phase. The larger the β_{12} is, the better the separation is. In most cases, β_{12} varies with concentration, but becomes unity at the plait point.

II. EXPERIMENTAL

Ternary liquid-liquid equilibrium data at 45°C. was obtained for the following three systems:

Benzene---n-Hexane--Acetonitrile

Benzene---Cyclohexane--Acetonitrile

n-Hexane--Cyclohexane--Acetonitrile

The acetonitrile used in this work was Fisher Scientific Company's reagent grade. The n-hexane, cyclohexane, and benzene were Phillips Petroleum Company's "pure" grade reported to be 99 mole % pure. These reagents were used without further purification because gas chromatographic Analysis revealed no significant impurities.

Originally, it was planned to determine the equilibrium data by analysing the compositions of the coexisting liquid phases by means of a quantitative chromatographic analysis. Several chromatography columns with different packings were tested, but none were capable of yielding a reproducable quantitative analysis for these ternary systems. However, it was found that a reproducable quantitative analysis could be obtained for the ratio of two of the components in the ternary mixture. Because of this analytical limitation, it was necessary to first determine the binodal curve and then locate tie lines by determining the ratio of these two components in each of the coexisting liquid phases.

To illustrate this technique refer to the ternary system

shown on Figure 4 comprised of components A, B, and C where components B and C are partially miscible. By chromatographic analysis the ratio of A to B can be determined in each of the coexisting liquid phases at equilibrium. Because each phase of the ternary mixture having a specified ratio of A to B lies on a line passing through the point C and a point on the AB side of the triangle corresponding to this ratio (points F and H), the lines CH and CF can be drawn. The intersection of these lines with the proper portion of the binodal curve then locates the tie line compositions E and G. Because different types of experiments are required for the determination of the binodal curve and for the determination of the tie lines, these subjects will be discussed separately.

Determination of the Binodal Curve

Three different methods for determining the binodal curve were used. Although only one method was found to be suitable for these systems, all three methods are discussed below. Titration Method: The titration method locates a point on the binodal curve representing the maximum solubility of a pure component in a mixture containing a known ratio of the other two components. This is done by titrating a known quantity of the binary mixture with the pure component until the solubility limit is reached. This end point is determined by the appearance of a second liquid phase. This process can be represented graphically and is shown on Figure 5. The composition of the

ternary mixture resulting from the titration of a mixture of
components A and B, represented by point D, with pure component
C lies on the line CD. As the titration proceedes, the point
representing the mixture moves toward C until the maximum
solubility of component C is reached at point E. Similarly,
pure C could be titrated with the mixture D until the solubility
limit represented by point F is reached. It is also possible
to locate points H and I by titrations involving pure B and a
solution of components A and C as represented by point G.
Points E, F, H, and I all lie on the binodal curve.

Because the equilibrium data were desired at a temperature
of 45° C., it was necessary to carry out the titration inside a
16" x 16" x 38" thermostated air bath with all manipulations
performed through glove ports located in the sides of the
thermostat. In addition to the difficulty of mechanical
manipulation, the rate of dissolution of the titrating liquid
was quite slow and the end point was uncertain. For these reasons
the titration method was abandoned after several futile attempts.
Cloud Point Method: In using the cloud point method one finds
the temperature to which a homogeneous solution of known
composition must be cooled before a second liquid phase is formed.
This temperature is refered to as the unmixing temperature or
the cloud point. This method is used almost exclusively for
determining binary liquid-liquid solubility data, because at a
given temperature there is only one saturated liquid phase
composition and the solubility curve of concentration versus

temperature is easily established. The corresponding solubility found for a ternary system, however, would be a three dimensional surface because at a given temperature the points representing saturated liquid solution lie along a curve, the binodal curve. The cloud point measurement gives the temperature at which a particular ternary solution becomes saturated with respect to a second liquid phase, however, we desire to know the saturated liquid compositions at a specified temperature. This can be accomplished by the following scheme which is illustrated by Figures 6 & 7. Several ternary mixture of known composition, all having the same ratio of components A and B, are prepared and their cloud points are determined. These mixtures lie along the line EC on Figure 7 and their cloud point temperatures are shown as curve E on Figure 6. A point on the binodal curve is determined by the intersection of the curve E on Figure 6 with the horizontal line corresponding to $t = 45°$ C. The complete binodal curve can be established by determining the cloud points of several other sets of ternary mixtures as represented by the lines DC and FC on Figure 7 with corresponding curves F and C on Figure 6.

The cloud point apparatus was quite simple and consisted of a heavy-walled glass tube having a flange and gasket closure. A copper-constantan thermocouple, which passed through the flange, was used together with a potentiometer to measure the temperature of the mixture. The whole tube assembly was immersed in a water bath provided with a heater and a cooling coil for temperature

control.

The cloud point of a given ternary mixture was determined by first heating the mixture until only one homogeneous liquid phase existed, then cooling this liquid phase slowly until a second liquid phase appeared. While this cooling process occured the tube was shaken regularly by hand so that there would be no temperature gradients within the liquid it contained. The cloud point was not easily determined because the solution often exhibited an opalescence which gradually intensified and became opaque as the temperature was lowered a few degrees. The opaqueness represents the formation of the second liquid phase, but because the change was gradual it was difficult to determine where opalescence ended and opaqueness began, and therefore the cloud point could be in error by as much as one or two degrees centigrade. This error in the temperature could cause considerable error in locating the binodal curve. Thus the cloud point method was considered insufficiently reliable and was abandoned.

The Modified Titration Method: This method was divised to eliminate the disadvantages of slow rate of dissolution and uncertain end point which were associated with the titration method, and can be regarded as a discrete, rather than a continuous, titration. A series of ternary mixtures having a specified ratio of two of the components and differing by regular mole percent increments of the third component were prepared and were equilibrated at the desired temperature and then examined

to determine the number of liquid phases present. For the purpose of illustration these mixtures are represented by points X_1, X_2, X_3, X_4 on Figure 8. Suppose that the mixture X_3 was a single homogeneous phase and mixture X_4 formed two liquid phases; now a point on the binodal curve has been bracketed. The bracketing process is continued by preparing a new mixture, $X_{3.5}$, lying halfway between X_3 and X_4 so that we will know whether the binodal curve passes between $X_{3.5}$ and X_3 or between $X_{3.5}$ and X_4.

Each sample was contained in a 5c.c. screw-cap vial for examination. Prior to making a series of samples, a sufficient quantity of binary solution of the desired composition was prepared by weighing out the components on an analytical balance. The first step in preparing a sample was to weigh the empty vial on the analytical balance. The balance was then adjusted to read the weight of the vial plus a predetermined quantity of the binary solution, and the binary solution was added to the vial by means of a syringe having a 26 gauge needle until the balance point was reached. The balance was then adjusted to read the weight of the vial and binary solution plus the weight of the third component necessary to form the desired ternary composition, and the third component was also added by means of a syringe until the balance point was reached. For a series of samples prepared from a given binary solution the composition of the third component varied by a regular increment of 1 mole percent. Usually about 8 to 10 samples were prepared for the

initial bracketing of one point on the binodal curve.

After preparing the samples, they were put in a rack and then kept in the rack in the thermostated box overnight at 45° C. with mechanical shaking to make sure equilibrium was reached. The temperature of the thermostated box was automatically controlled by a Thermistep Model 63 Temperature Controller so that the temperature variation of the thermostat was less than ± 0.05° C. After the equilibrium state was reached, the samples were observed through an acrylic plastic pane in the front of the thermostat to find two neighboring samples one of which was homogeneous , and the other heterogeneous. The heterogeneous phase was identified by the appearance of tiny droplets. The droplets appeared on the bottom of the vial if the nascent phase was the more dense phase, and in the meniscus if the nascent phase was lighter.

After these two bracketing samples were identified, another sample whose mole percentage of C lay halfway between these samples was prepared in the same manner described above. This sample was equilibrated and then observed to determine whether it was homogeneous or heterogeneous. A point on the binodal curve was then bracketed to within 0.5 mole % of the third component. The bracketing process was not continued because experimental errors become relatively more important.

There are two errors which could affect the results of this experiment. One is evaporation during sample preparation. The other is the limitation of obtaining the exact sample weight

because of the drop-wise method of sample preparation. The
evaporation error can be minimized by putting the component of
higher density into the vial before the component of lower
density. This will tend to equalize the evaporation errors
associated with each weighing, as evaporation would occur only
across the air-liquid interface and each liquid would be exposed
to the air for approximately the same time. The weight loss of
either component C or the mixture of components A and B due to
evaporation was determined experimentally to be about 0.003 gram.
The weight of each drop from the syringe needle was measured and
found to be about 0.002 gram. These two experimental errors can
be make to oppose each other by preparing the sample in such a
manner that the sample is always overweight by zero to one drop.
An error analysis shows that if both component C and the mixture
weights were subject to evaporation errors of 0 to 0.003 grams
and weighing errors of 0 to 0.004 grams, that the total error
involved in this experiment amounts to about 0.02 to 0.2 mole
percent for each component depending upon its concentration
level. Even if this error adds to the bracketing uncertainty of
$\pm$ 0.25 mole %, the total uncertainty is still within $\pm$ 0.5 mole
%.

The results of the modified titration method are presented
in Table 1, and plotted on Figures 11, 12, and 13. The data
points represent the averaged composition of the two braketing
samples which differed by 0.5 mole % C. On Figures 11, 12, and
13 the points are drawn to indicate this experimental uncertainty.

Table 1   The Data Points for the Binodal Curve

(1)   the system of Benzene, n-Hexane, and Acetonitrile

mole percent of n-Hexane	mole percent of Benzene	mole percent of Acetonitrile
9.40 %	0.00 %	90.60 %
14.75 %	8.52 %	76.72 %
25.00 %	15.00 %	60.00 %
45.00 %	17.87 %	37.12 %
60.00 %	14.00 %	26.00 %
69.00 %	10.85 %	20.15 %
75.25 %	8.04 %	16.71 %
84.00 %	3.20 %	12.80 %
87.50 %	1.25 %	11.25 %
89.60 %	0.00 %	10.40 %

(2)   the system of Benzene, Cyclohexane, and Acetonitrile

mole percent of Cyclohexane	mole percent of Benzene	mole percent of Acetonitrile
11.40 %	0.00 %	88.60 %
17.50 %	8.25 %	74.25 %
32.00 %	13.60 %	54.40 %
48.00 %	15.60 %	36.40 %
51.00 %	15.92 %	33.07 %
60.25 %	15.90 %	23.85 %
71.00 %	13.05 %	15.95 %
74.00 %	11.70 %	14.30 %
81.00 %	7.60 %	11.40 %
84.25 %	5.12 %	10.63 %
90.10 %	0.99 %	8.91 %
91.20 %	0.00 %	8.80 %

(3)   the system of n-Hexane, Cyclohexane, and Acetonitrile

mole percent of Acetonitrile	mole percent of Cyclohexane	mole percent of n-Hexane
8.80 %	91.20 %	0.00 %
9.75 %	72.20 %	18.25 %
10.25 %	44.87 %	44.87 %
10.75 %	17.75 %	71.40 %
90.60 %	0.00 %	9.40 %
89.90 %	2.20 %	8.08 %
89.25 %	5.57 %	5.37 %
88.50 %	9.20 %	2.30 %
88.60 %	11.40 %	0.00 %

Determination of Tie Lines

For the tie line determination a heterogeneous ternary mixture of known composition was prepared using the analytical balance and was placed in a 20 c.c. pyrex equilibrium cell which was sealed by a flange and gasket closure. The equilibrium cell was kept in the previously described thermostated box overnight and was shaken mechanically to make sure the equilibrium state was obtained. The two coexisting liquid phases were then sampled for gas chromatographic analysis.

The most obvious way to sample for chromatographic analysis is to insert the needle of a syringe into each phase, withdraw the sample, and inject it into the gas chromatograph directly. This procedure was unsatisfactory for sampling the equilibrated liquid phases under conditions used in this work. These liquid phases were saturated at 45° C. and any cooling would result in the formation of a second liquid phase. Therefore if cooling occurs any time during sampling, the sample injected into the chromatograph will not necessarily be the same composition as the sampled phase. In order to circumvent this problem an indium incapsulation sampling technique was used to prepare samples of the saturated liquid phases for the chromatographic analysis.

The indium incapsulation technique was developed by the Varian Aerograph Company and the sampling system marketed by them is called the Inductor, Model 695. The Inductor consists of

three components: the encapsulation material, the introduction chamber, and the control system. The sample is encapsulated in a length of tubing made of indium, which is a soft, ductile, and malleable metal of 156° C. melting point. Because of these special properties, the tubing is capable of being pinched, and forming a leak-proof closure with a specially designed swaging tool. The sample is contained within a capsule formed by pinching off both ends of a section of tubing. A heated introduction chamber accepts the indium capsule, melts it, and vaporizes the sample. Then the sample is carried into the gas chromatograph by carrier gas which flows continuously through the introduction chamber. The control system includes a powerstat for adjusting the temperature of the introduction chamber and an indicating thermocouple which measures its temperature. In this experiment the temperature was maintained at 200° C., the carrier gas was nitrogen, the size of the indium tubing was 0.06" O.D. x 0.03" I.D..

To prepare the indium capsules for chromatographic analysis, a section of hypodermic tubing was inserted into one end of an indium tube, and another section of hypodermic tubing fitted with a Luer hub was inserted into the other end. Both junctions were sealed by heating in order to prevent leakage. This assembly was attached to a hypodermic syringe through the Luer hub and the section of indium tubing was filled by drawing liquid into the syringe. After the section of indium tubing was filled, it was cut into small capsules with the swaging tool, and taken out of the thermostat. Each capsule contained

approximately 1 microliter. While sampling, only the lower section of the hypodermic tubing was immersed in the liquid sample in order to keep the indium tube from directly contacting the liquid. Otherwise, the adiabatic vaporization of the liquid adhering to the outside of the indium tubing would decrease its temperature. This temperature decrease would cause the saturated homogeneous liquid inside the tubing to separate into two phases. As a result the sample in each capsule might not represent the equilibrium composition. Before this sampling procedure was used considerable scattering of the peak area ratios was found. After using the specially designed sampling system the scattering was reduced considerably.

The chromatograph used for this analysis was a Varian Aerograph Model 600 D Gas Chromatograph, associated with a Sargent Model SR Recorder and a Disc Integrator, Model 204. The chromatographic column was a 1/8" O.D. stainless steel tube 5 feet long, which was packed with 20% DEGS on 60/80 Chrom W for the n-hexane--benzene--acetonitrile and cyclohexane--benzene--acetonitrile systems. A similar column packed with 5% SE-30 on 60/80 A/W DMCS Chrom W was used for the n-hexane--cyclohexane --acetonitrile system. The columns and their packings were supplied by the Varian Aerograph Co. The detector in this chromatograph was a flame ionization detector.

As shown in Figure 4, the sample taken from one phase was rich in component C and taken from the other phase was rich in component B. Since the ratio of component A to B was used to

determine the ternary composition, we assumed the value of the A, B ratio was independent of the sample size and independent of the presence of component C. Although this assumption is routinely made in many chromagraphic studies and appears to be well justified, the following experiment was performed as a test of its validity. Samples were made by mixing a solution which consisted of 30 mole % bezene and 70 mole % acetonitrile with different quantities of n-hexane. Then the samples were placed in indium capsules and introduced into the chromatograph through the Inductor system. The averages of several chromatographic analysis are shown below where it can be observed that the peak area ratio of acetonitrile to benzene is indeed independent of the n-hexane concentration.

mole % of acetonitrile-benzene solution	mole % of n-hexane	peak area ratio of A, to B
100 %	0 %	2.35
90 %	10 %	2.35
70 %	30 %	2.35
10 %	90 %	2.38

Since the ratio of two peak areas was used to determine composition, it was necessary to prepare a calibration curve relating the ratio of peak area to the mole fraction of the two components. This calibration was prepared from various samples of known composition, which were contained in indium capsules and analyzed chromatographically at the specified operating conditions. The calibration curves for the benzene--acetonitrile

system and for the n-hexane--cyclohexane system are shown on Figure 9 and Figure 10. Since the deviation of the chromatographic peak area ratio relative to its average value was from 0 to $\pm$ 3 % for these analysis, an arithmatic average was taken of five duplicate measurements to determine the calibration curves.

For each ternary system, four different mixtures of known overall composition were equilibrated and sampled. For each phase the peak area ratios of two components resulting from the chromatographic analysis of these samples were obtained. Because of the experimental deviation of 2-4% for these ratios an arithmatic average was taken of five duplicate measurements to determine the peak area ratio. From the peak area ratios the mole ratios of two of the components were determined by means of the calibration curve, and the equilibrium composition was then located with the help of the binodal curve by the method previously described.

The equilibrium compositions represent two ends of a tie line. Because the overall composition of the mixtures was known, the experimental results can be checked by the mass balance relation, i.e. the ends of a tie line and the initial composition should be connected by a straight line. The experimental results showed that this mass balance relation was checked within the experimental deviations. The tie line data for these three systems are presented in Table 2, and plotted on Figures 11, 12, and 13. The overall compositions are also shown on these Figures

to illustrate the material balance consistency check.

Table 2 Tie Line Compositions

(1) Benzene--n-Hexane--Acetonitrile system

n-Hexane-rich phase			Acetonitrile-rich phase		
mole % of Benzene	mole % of n-Hexane	mole % of Acetonirtile	mole % of Benzene	mole % of n-Hexane	mole % of Acetonitrile
0.0	89.6	10.4	0.0	9.4	90.6
5.5	79.9	14.6	3.1	10.8	86.1
8.2	75.0	16.8	5.0	12.0	83.0
10.8	69.0	20.2	7.3	13.7	79.0
14.5	59.3	26.2	11.6	18.4	70.0

(2) Benzene--Cyclohexane--Acetonitrile system

Cyclohexane-rich phase			Acetonitrile-rich phase		
mole % of Benzene	mole % of Cyclohexane	mole % of Acetonitrile	mole % of Benzene	mole % of Cyclohexane	mole % of Acetonitrile
0.0	91.2	8.8	0.0	11.4	88.6
4.9	84.8	10.3	3.3	12.7	84.0
7.1	81.6	11.3	4.8	13.8	81.4
10.5	76.3	13.4	7.0	15.7	77.3
15.8	53.0	31.2	12.0	25.8	62.2

(3) n-Hexane--Cyclohexane--Acetonitrile

n-Hexane-rich phase			Acetonitrile-rich phase		
mole % of n-Hexane	mole % of Cyclohexane	mole % of Acetonitrile	mole % of n-Hexane	mole % of Cyclohexane	mole % of Acetonitrile
0.0	91.2	8.8	0.0	11.4	88.6
17.9	72.3	9.8	2.3	9.3	88.4
35.8	54.2	10.0	4.2	7.0	88.6
50.8	38.6	10.6	5.4	5.4	89.2
72.2	17.0	10.8	7.4	3.0	89.6
89.6	0.0	10.4	9.4	0.0	90.6

III. PREDICTION OF TERNARY LIQUID-LIQUID EQUILIBRIA

In the former section the liquid-liquid equilibrium compositions of the following three systems were determined experimentally.

Benzene--n-Hexane--Acetonitrile

Benzene--Cyclohexane--Acetonitrile

Cyclohexane--n-Hexane--Acetonitrile

Four tie lines were determined in each system. In this section, we will predict the liquid-liquid equilibrium composition of these systems from binary information and compare the results with the experimental data.

The Calculation Procedure for Predicting Ternary Liquid-Liquid Equilibria:

At constant temperature and pressure, the equilibrium condition for a liquid-liquid system has been shown to be the equality of the activity of each component in each liquid phase. Since a ternary system has three components, the condition of equilibrium is that the system obeys the following three equations.

$$x_i' \gamma_i' = x_i'' \gamma_i'' \qquad (i = 1, 2, 3) \qquad (12)$$

Once an activity coefficient equation has been selected and its parameters determined, it can be substituted into equation(12) yielding a system of three equations containing six unknown compositions. Of these six unknowns, two may be eliminated by the conditions

$$\Sigma \, x_i' \; = \; 1$$

and   (13)

$$\Sigma \, x_i'' \; = \; 1$$

If the composition of one of the components, the independent variable, is arbitrarily fixed, it is theoretically possible to solve these three equations for the other compositions.

The solution of this set of equations for the tie line compositions was accomplished by means of a Newton-Raphson iteration method using the IBM 360/50 computer. The computer program, written by Joy(7), calculates tie lines at regular preassigned increments of the independent variable x_1'. There is no guarantee that the Newton-Raphson method will converge, however, when good initial estimates of all the variables are available, the method usually converges very rapidly. For making good initial estimates for each tie line computation, Chen(8) suggested that the tie line computation start from the 2-3 binary edge and utilize the solvent selectivity for the initial estimate. The solvent selectivity, defined previously by equation (11), can be expressed in terms of activity coefficients with the help of equation (12)

$$\beta_{12} \; = \; \gamma_2' \, \gamma_1'' \; / \; \gamma_2'' \, \gamma_1'$$ (14)

For the calculation of the first tie line it is assumed that the values of x_2' and x_2'' are the same as those at the 2-3

binary edge. Because x_1' is the independent variable its value is assigned, and the value of x_1'' is then calculated from x_1', x_2', and x_2'' using the value of β_{12} evaluated at the binary edge. The initial estimates of x_3' and x_3'' for the first tie line are obtained by applying equation (13). The value of β_{12} at the 2-3 binary edge can not be obtained from equation (11) directly because x_1' and x_1'' equal zero, however it can be obtained from equation (14) because the limiting values of γ_1' and γ_1'' as given by the ternary activity coefficient equation exist as x_1' and x_1'' tend to zero.

After the first tie line had been calculated, the initial estimates for succeeding tie lines were obtained from the compositions and the solvent selectivity of previously calculated tie lines using an extrapolation method.

The NRTL Equation: There are several activity coefficient equations which have been developed, however, the NRTL activity coefficient equation was used in this prediction because it has been shown to be capable of describing partially miscible systems, and because it requires only binary information. The NRTL equation for a binary system of component 1 and 2 is shown below:

$$\ln \gamma_1 = x_2^2 \left(\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right)$$

$$\ln \gamma_2 = x_1^2 \left(\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right) \tag{15}$$

where

$$G_{12} = \exp(-\alpha_{12}\,\tau_{12})$$

$$G_{21} = \exp(-\alpha_{12}\,\tau_{21})$$

In this equation, x_1 and x_2, are the mole fractions in one liquid phase, Y_1 and Y_2 are the activity coefficients, and α_{12}, τ_{12}, τ_{21} are the three parameters, which characterize the binary system.

The NRTL activity coefficient equation for component i in a ternary system is shown below:

$$\ln Y_i = \frac{\sum\limits_{j=1}^{3}\tau_{ji}G_{ji}x_j}{\sum\limits_{l=1}^{3}G_{li}x_l} + \sum\limits_{j=1}^{3}\frac{x_j G_{ij}}{\sum\limits_{l=1}^{3}G_{lj}x_l}\left(\tau_{ij} - \frac{\sum\limits_{Y=1}^{3}x_r\tau_{rj}G_{rj}}{\sum\limits_{l=1}^{3}G_{lj}x_l}\right) \quad (16)$$

where

$$G_{ji} = \exp(-\alpha_{ji}\,\tau_{ji}), \quad \text{and} \quad \alpha_{ji} = \alpha_{ij}$$

This equation contains nine parameters α_{12}, τ_{12}, τ_{21}, α_{13}, τ_{31}, τ_{13}, α_{23}, τ_{23} and τ_{32}. The first three parameters are the same as those in the binary NRTL equation for the 1-2 system, the second three are the same as those in the binary NRTL equation for the 1-3 system, the third three are the same as those in the binary NRTL equation for the 2-3 system.

Now we have the computer program for predicting liquid-liquid equilibrium data and we have chosen the activity coefficient equation. The parameters for this activity coefficient equation will be determined in following section.

Binary NRTL Parameters

The parameters of the following binary systems were necessary for the prediction of tie lines for these three ternary systems.

n-Hexane--Benzene

Cyclohexane--Benzene

Cyclohexane--n-Hexane

Benzene--Acetonitrile

n-Hexane--Acetonitrile

Cyclohexane--Acetonitrile

The first four binary systems are completely miscible systems for which NRTL parameters are tabulated by Renon(3). He determined these parameters from vapor-liquid equilibrium data reported in the literature using a nonlinear least-squares computer program to minimize the sum-of-squares of deviations in total pressures plus the sum-of-squares of deviation in vapor-phase mole fraction for all experimental data points. The values obtained from Renon's Thesis are tabulated in Table 3. The last two systems are partially miscible systems for which the parameters are not available in Renon's Thesis. These parameters were determined by three different methods as described in the following sections.

Parameters from Total Pressure Data: The total pressures of the n-hexane--acetonitrile and cyclohexane--acetonitrile systems were determined at 45° C. for several liquid compositions by Huang(9), who also used these data to calculate the parameters

of the binary NRTL equation. He used a least squares program to determine the three parameters by minimizing the sum-of-squares of deviations in pressure for all experimental data points. The values obtained from his Thesis are tabulated in Table 3.

Parameters from Mutual Solubility Data: These acetonitrile-hydrocarbon systems were classified by Renon(3) as mixtures of saturated hydrocarbons with polar nonassociated liquids. For systems of this type Renon suggests that α be set equal to 0.2 if insufficient data are available for evaluating all three parameters.

For these binary partially miscible systems, the condition of isothermal liquid-liquid equilibrium gives the following two equations:

$$x_1' \, \gamma_1' \;\; = \;\; x_1'' \, \gamma_1'' \tag{17}$$

$$x_2' \, \gamma_2' \;\; = \;\; x_2'' \, \gamma_2'' \tag{18}$$

where γ_1 and γ_2 are activity coefficients. When the three parameter NRTL activity coefficient equation is used, γ_1 and γ_2 are functions of these three parameters and the concentrations x_1' and x_1''. Substituting the known mutual solubility data into equation (17) and (18), we obtain two equations in three unknown parameters. By setting the parameter α equal to 0.2, according to Renon's rules, these two equations can be solved for the other two parameters τ_{12} and τ_{21}. Because these two equations are

complicated nonlinear algebric equations, they can not be solved
by usual calculating procedure. The values of τ_{12} and τ_{21} are
found by using an optimal search technique such that the following
function is minimized,

$$((x_1' \ \gamma_1' \ - \ x_1'' \ \gamma_1'')^2 \ + \ (x_2' \ \gamma_2' \ - \ x_2'' \ \gamma_2'')^2) \tag{19}$$

The Simplex optimal search technique was used in this problem.
The computer program for the Simplex method was written by
Chen(10). In this program first the initial estimates of τ_{12}
and τ_{21} were supplied, then the computer searches for the optimal
value of τ_{12} and τ_{21} along the direction of minimizing equation
(19). After several iterations, the optimal values of τ_{12} and
τ_{21} were found. These values of τ_{12} and τ_{21} are tabulated in
Table 3.

Parameters from Mutual Solubility and Total Pressure Data:
Instead of using $\alpha = 0.2$, as suggested by Renon, the parameters
τ_{12} and τ_{21} for these two systems were next calculated from the
mutual solubility data for a series of α's, each differing by a
0.01 increment, for α between 0.1 and 0.4. For each α the
calculation is the same as described above. For each value of
α and the corresponding calculated values of τ_{12} and τ_{21} the
total pressures were calculated for every liquid composition of
Huang's data. Then the calculated total pressures were compared
with the experimental total pressures for all data points. The
total error was obtained from the following formula:

$$\sum_{n} (P_{cal.} - P_{exp.})^2 \tag{20}$$

The best set of parameters were those for which equation (20) was minimized. The values of α and corresponding τ_{12} and τ_{21} are tabulated in Table 3. This method forces the parameters to represent the mutual solubility data, but also gives weight to the total pressure data.

Prediction Results

Now we have obtained all binary parameters of the NRTL equation for predicting the three ternary liquid-liquid systems. The parameters for miscible binary pairs are obtained from Renon's Thesis, and the parameters for partially miscible pairs are estimated by the three different methods as just described. For each ternary system three different prediction results are obtained by using sets of parameters estimated by the three different methods. The experimental data and the prediction results are plotted on Figures 14, 16, and 18. To avoid making the figures confusing, experimental and predicted tie lines are not plotted and only the binodal curves are shown. To compare the difference between the predicted and experimental tie line data, solvent selectivity is plotted on Figure 15, 17, and 19 for each system respectively. Each point on these figures represents one tie line. Is should be noted that because it is defined in terms of ratios of compositions, the solvent

selectivity is very sensitive to small changes in tie line compositions. Therefore a comparison of calculated and experimental solvent selectivity is a stringent test of the prediction results.

Figures 14, 16, and 18 show that binary mutual solubility data predicted from total pressure data does not agree with that data from liquid-liquid solubility experiments. When the NRTL parameters estimated from total pressure data were used for predicting the ternary systems, the solubility data predicted from total pressure data were used as the starting point for calculating the first tie line. When the NRTL parameters estimated from solubility data were used for predicting the ternary system, the solubility data from liquid-liquid solubility experiments were used as the starting point for calculating the first tie line.

Benzene(1)--n-Hexane(2)--Acetonitrile(3) system: Figure 14 shows that the binodal curve from solubility data and from combined solubility and total pressure data are superimposed and show poor agreement with the experimental curve. Although the binary solubility data predicted from total pressure data do not agree with experimental solubility data, the binodal curve predicted from total pressure data shows good agreement with the experiment data. Figure 15 shows that solvent selectivity predicted from total pressure data is better than that from solubility data and reasonably good agreement with experimental data is obtained.

Benzene(1)--Cyclohexane(2)--Acetonitrile(3): Figure 16 also
shows that although the binary solubility data predicted from
total pressure data do not agree with experimental solubility
data, the binodal curve predicted from total pressure data shows
better agreement with experimental data than that from solubility
data or from combined solubility and total pressure data. The
binodal curve predicted from solubility data is a little better
than from the combined solubility and total pressure data.
Figure 17 shows again that solvent selectivities predicted from
total pressure data are better than those predicted from the
other parameters, but they are only in fair agreement with
experimental values.

n-Hexane(1)--Cyclohexane(2)--Acetonitrile(3): Figure 18 shows
the right hand binodal curves from the different methods agree
with experimental data reasonably well. The left hand binodal
curves predicted from solubility data and from the combined
solubility and total pressure data are superimposed with the
experimental binodal curve, but the binodal curve predicted from
total pressure data does not agree very well with the experi-
mental curve because the boundary points do not agree with the
binary solubility data. On Figure 19 the agreement between
predicted and experimental solvent selectivity appears to be poor
until it is noted that the ordinate scale is a ten fold
magnification over the scale in Figures 15 and 17. Actually, the
deviations between the experimental curve and the prediction
curves are smaller than those of the other two systems. The

experimental value of the solvent selectivity ranges from about 0.95 to 1.35 while the predicted values range from about 1.02 to 1.15. Again the total pressure data produce the best prediction although the difference between the predictions is less pronounced than for the other two systems. This appears to agree with the analysis of Joy and Kyle(4) that prediction results for type II systems are less sensitive to errors in the parameters than are the type I systems.

Discussion

By using total pressure data for evaluating the parameters of the partially miscible binary, the predicted values show better agreement than that by using solubility data. A combining of total pressure and mutual solubility data, however, does not improve the prediction over that from solubility data, which implys forcing the parameters to fit mutual solubility data is not justified. Therefore the total pressure data for evaluating the parameters for partially miscible systems are prefered if they are available.

It is generally accepted that ternary vapor-liquid equilibrium can be predicted with reasonable confidence from binary information. In fact, Van Winkle and Holmes(2) tested 19 systems and state that of 262 predicted ternary vapor phase mole fractions 92% differed from the experimental values by less than 0.02 mole fraction. This test was performed simply by calculating vapor phase mole fractions at the same liquid phase

compositions as the experimental data points. Unfortunately, for ternary liquid-liquid equilibria unless the binodal curve is predicted perfectly the predicted and experimental compositions is the second liquid phase can not be compared at identical compositions in the first liquid phase. Therefore, in order to obtain an evaluation comparable to that of Van Winkle and Holmes it is necessary to compare predicted and experimental data on a solvent-free basis. Such a comparison seems reasonable because it is the solvent-free distribution relationship which determines the number of stages in an extraction process.

The prediction results for the three ternary systems when evaluated on a solvent-free basis possess the same degree of precision as the results of the vapor-liquid predictions reported by Van Winkle and Holmes. Both type I systems showed average deviations less than 0.02 mole fraction, while the type II system showed an average deviation of 0.03 mole fraction as shown in Table 4.

Table 3   the Parameters of the Binary NRTL Equation

(A)   Completely Miscible System (from Renon (3))

binary system	α_{12}	τ_{12}	τ_{21}
Benzene(1)--n-Hexane(2)	0.3	0.3196	0.1361
Benzene(1)--Cyclohexane(2)	0.3	0.2796	0.2009
Cyclohexane(1)--n-Hexane(2)	0.3	0.8780	-0.7150
Benzene(1)--Acetonitrile(2)	0.3	0.7264	0.3750

(B)   Partially Miscible System

1.   Parameter evaluated from total Pressure Data(from Huang(9))

n-Hexane(1)--Acetonitrile(2)	0.3720	2.1336	1.9528
Cyclohexane(1)--Acetonitrile(2)	0.2659	1.8976	1.5245

2.   Parameters evaluated from mutual Solubility Data

n-Hexane(1)--Acetonitrile(2)	0.2000	1.7208	1.5409
Cyclohexane(1)--Acetonitrile(2)	0.2000	1.8467	1.4080

3.   Parameters evaluated from combined solubility and total Pressure Data

n-Hexane(1)--Acetonitrile(2)	0.1900	1.6940	1.5329
Cyclohexane--Acetonitrile(2)	0.1160	1.8962	1.1170

Table 4   Comparison of predicted and experimental Phase Compositions

(1)   Benzene--n-Hexane--Acetonitrile system

Benzene in n-Hexane-rich phase on n-Hexane-free basis	Benzene in n-Hexane-poor phase on n-Hexane-free basis		
	Experimental	Predicted from total pressure data	Predicted from solubility data
0.000	0.0000	0.0000	0.000
0.273	0.0347	0.0420	0.031
0.328	0.0568	0.0615	0.044
0.348	0.0846	0.0730	0.050
0.356	0.1422	0.0890	0.052
Absolute Average Error		0.0192	0.0353

(2)   Benzene--Cyclohexane--Acetonitrile system

Benzene in Cyclohexane-rich phase on Cyclohexane-free basis	Benzene in Cyclohexane-poor phase on Cyclohexane-free basis		
	Experimental	Predicted from total pressure data	Predicted from solubility data
0.000	0.0000	0.000	0.000
0.322	0.0378	0.046	0.039
0.386	0.0577	0.065	0.055
0.439	0.0830	0.090	0.075
0.336	0.1617		0.083
Absolute Average Error		0.008	0.022

(3)   n-hexane--Cyclohexane--Acetonitrile system

n-Hexane in Acetonitrile-poor phase on Acetonitrile-free basis	n-Hexane in Acetonitrile-rich phase on Acetonitrile-free basis	
	Experimental	Predicted from total pressure or from solubility data
0.000	0.000	0.0000
0.178	0.198	0.213
0.398	0.375	0.405
0.568	0.500	0.550
0.809	0.712	0.735
1.000	1.000	1.000
Absolute Average Error		0.029

ACKNOWLEDGEMENTS

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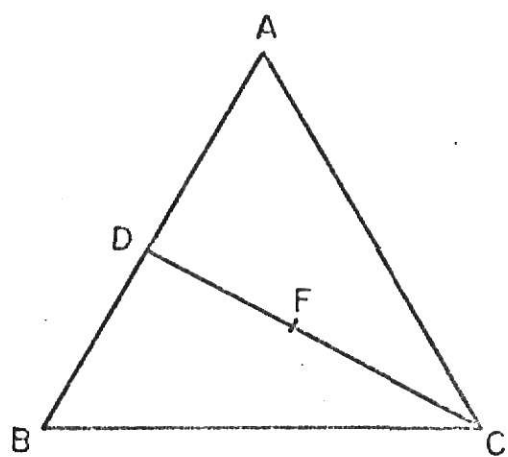
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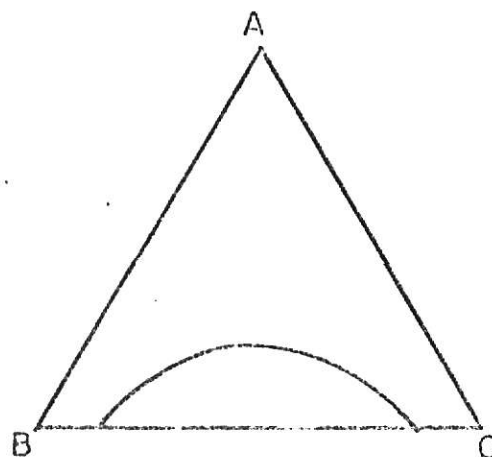
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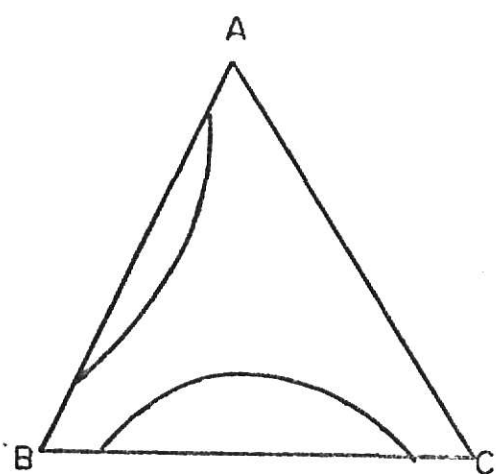
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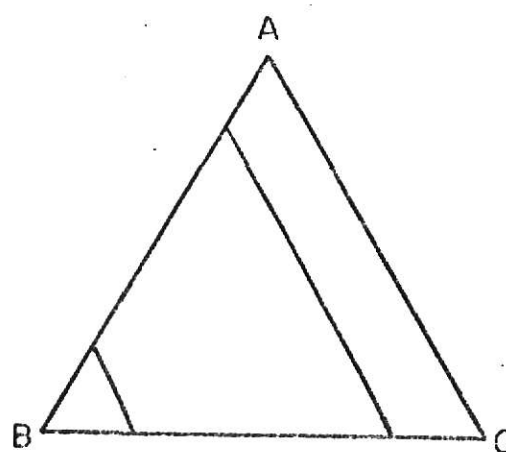
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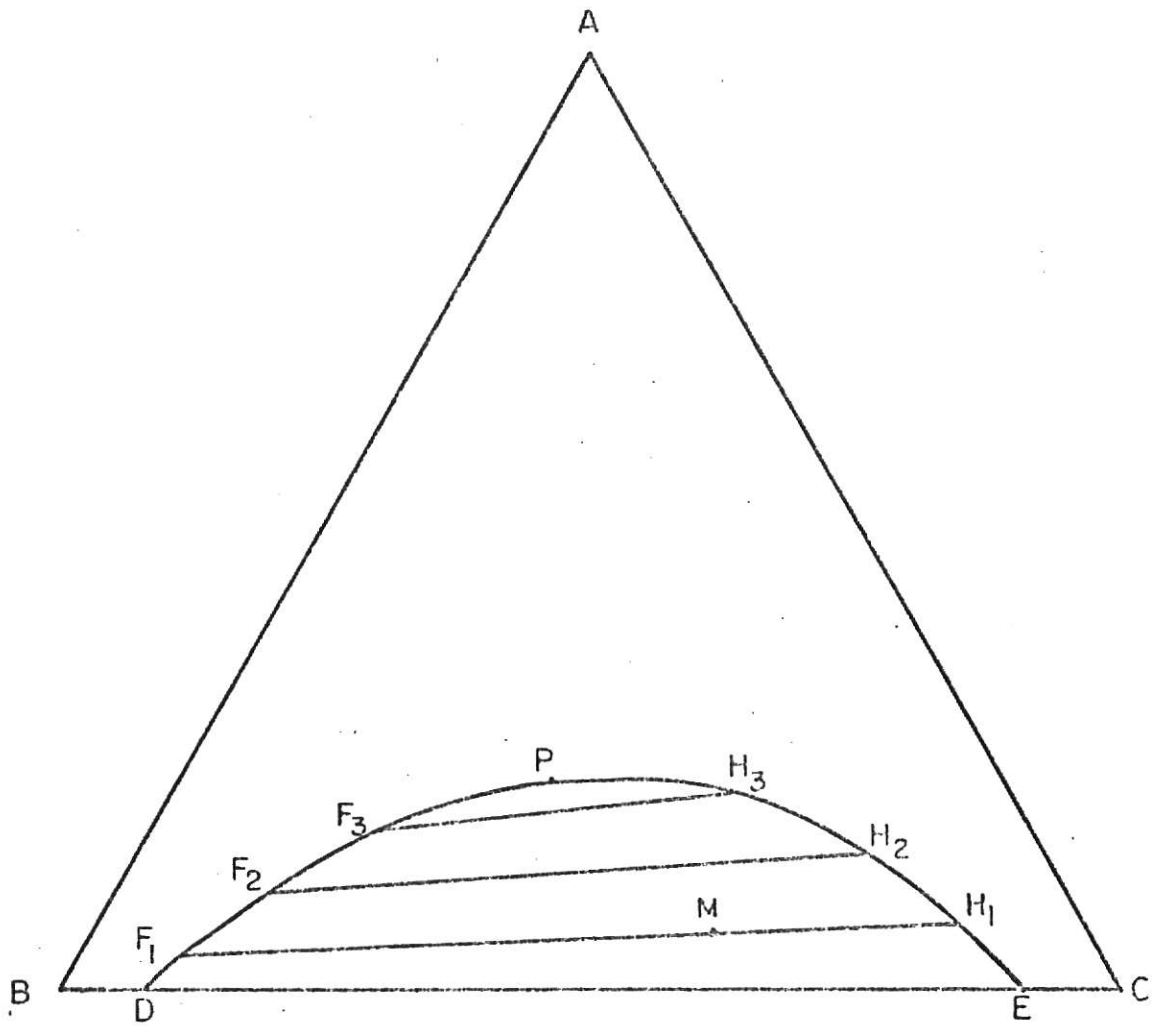
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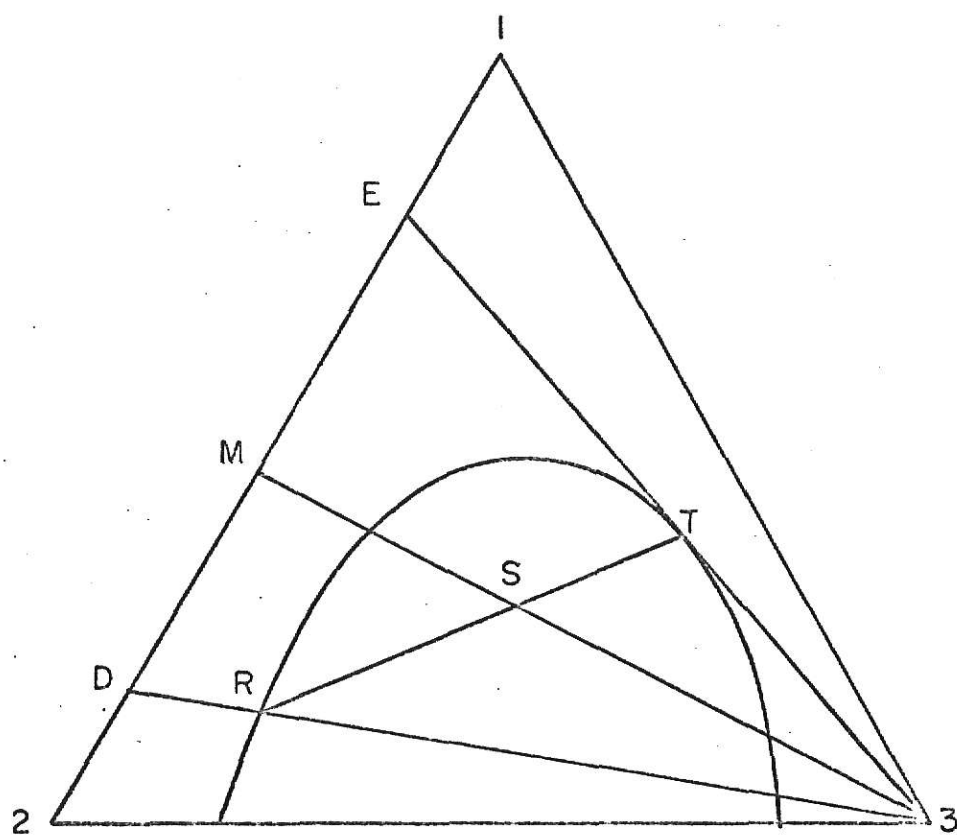
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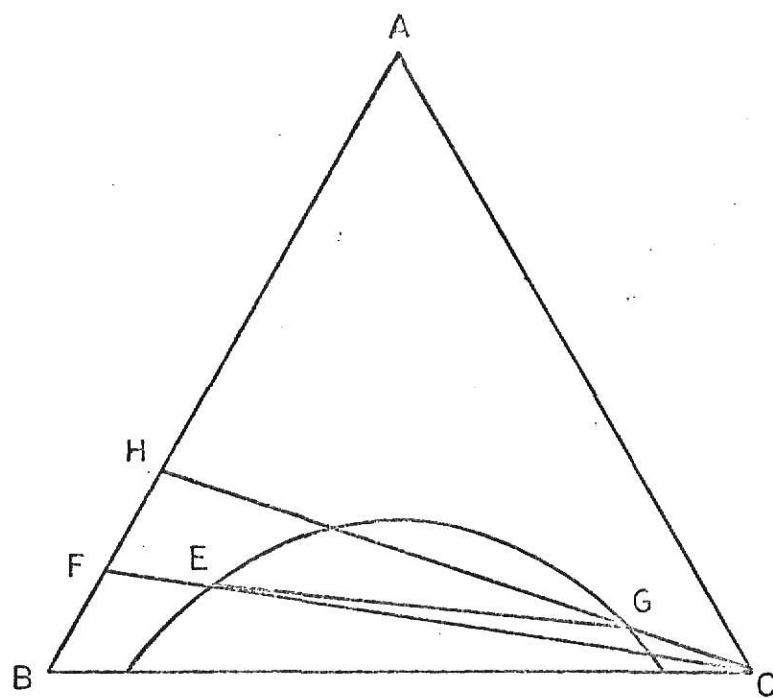
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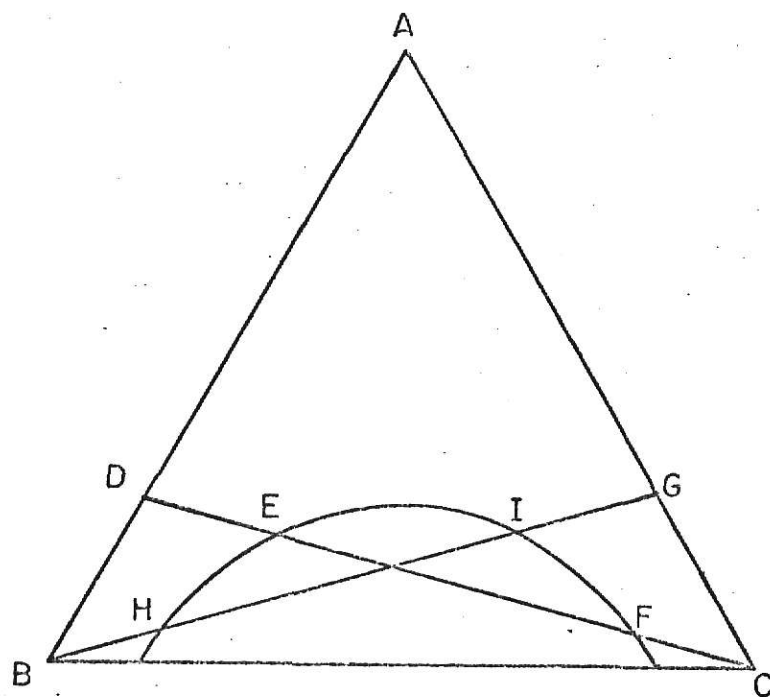
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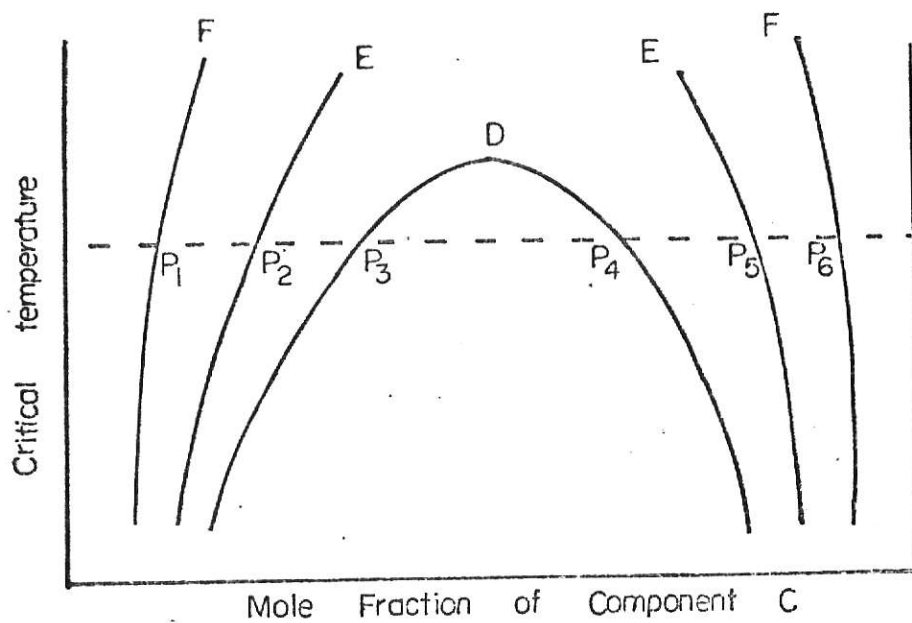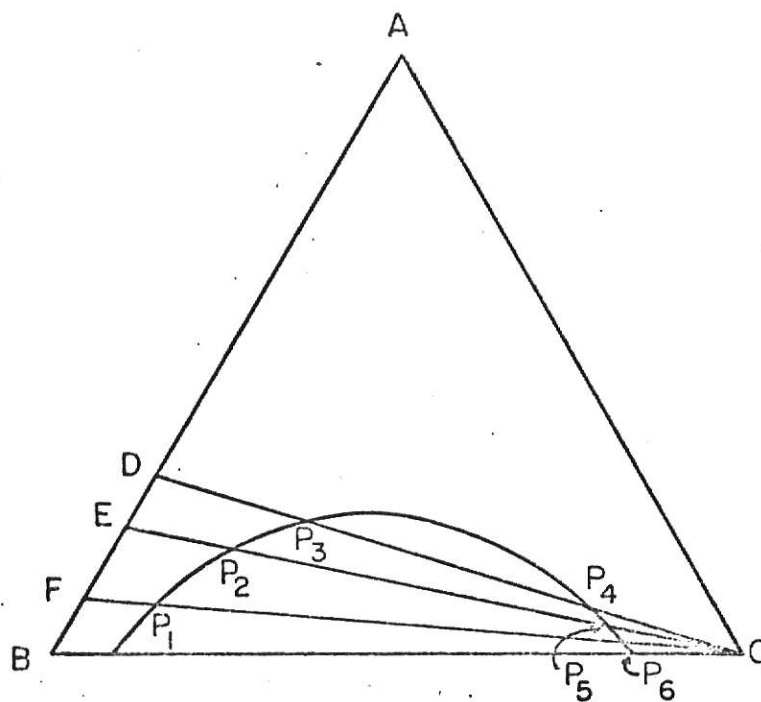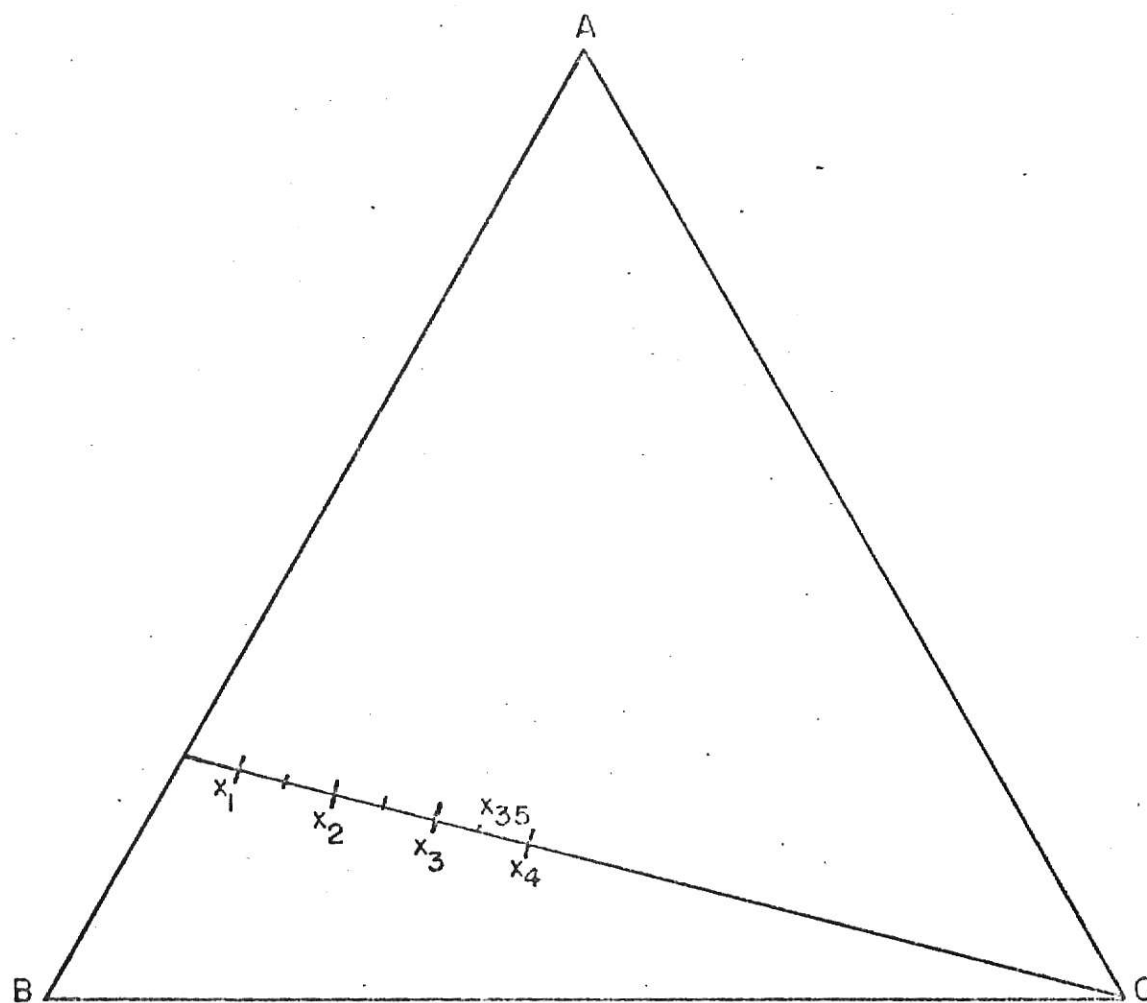
Figure 6

Figure 7

Figure 8
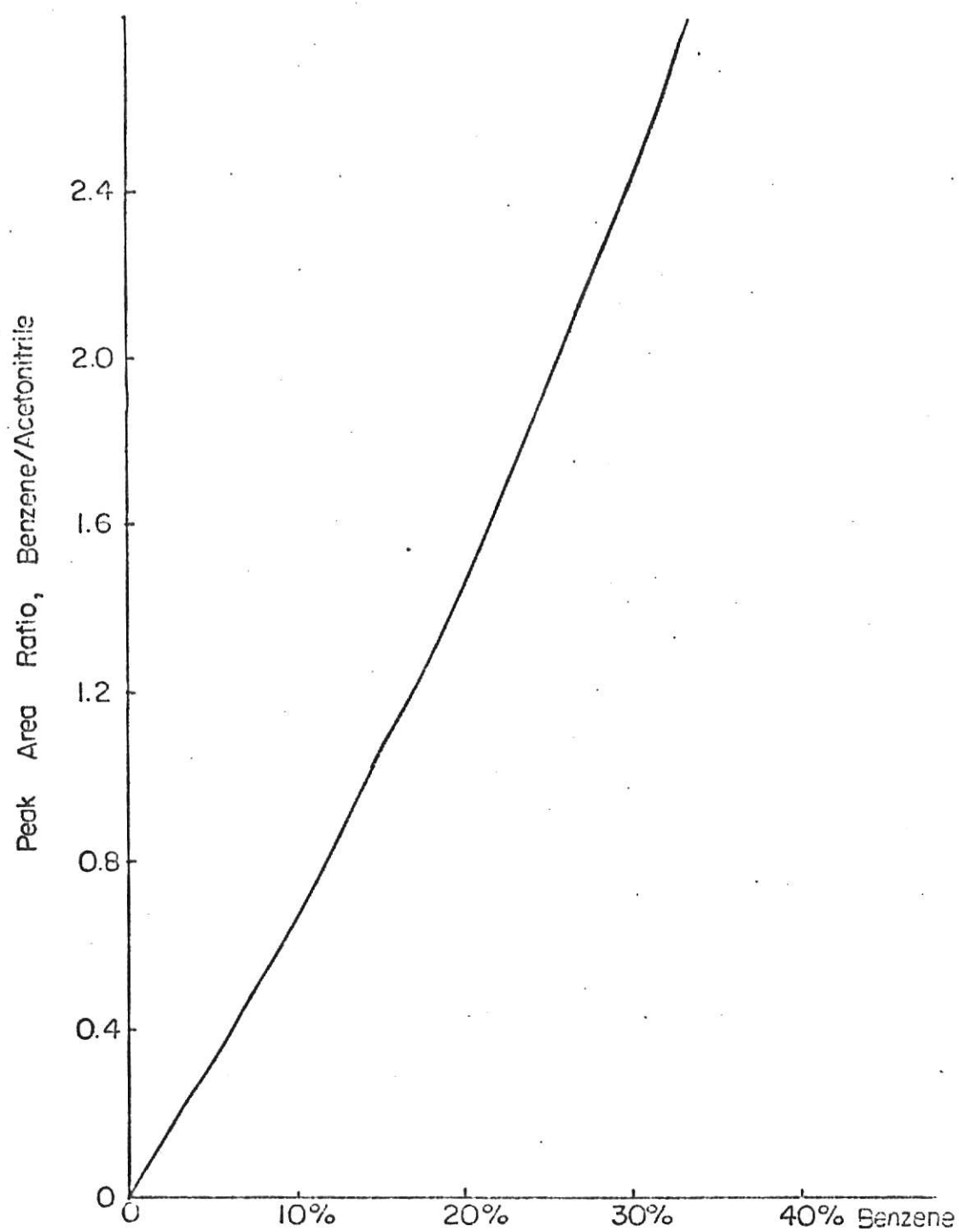
Fig. 9. Gas Chromatograph Calibration Curve for Benzene — Acetonitrile system.
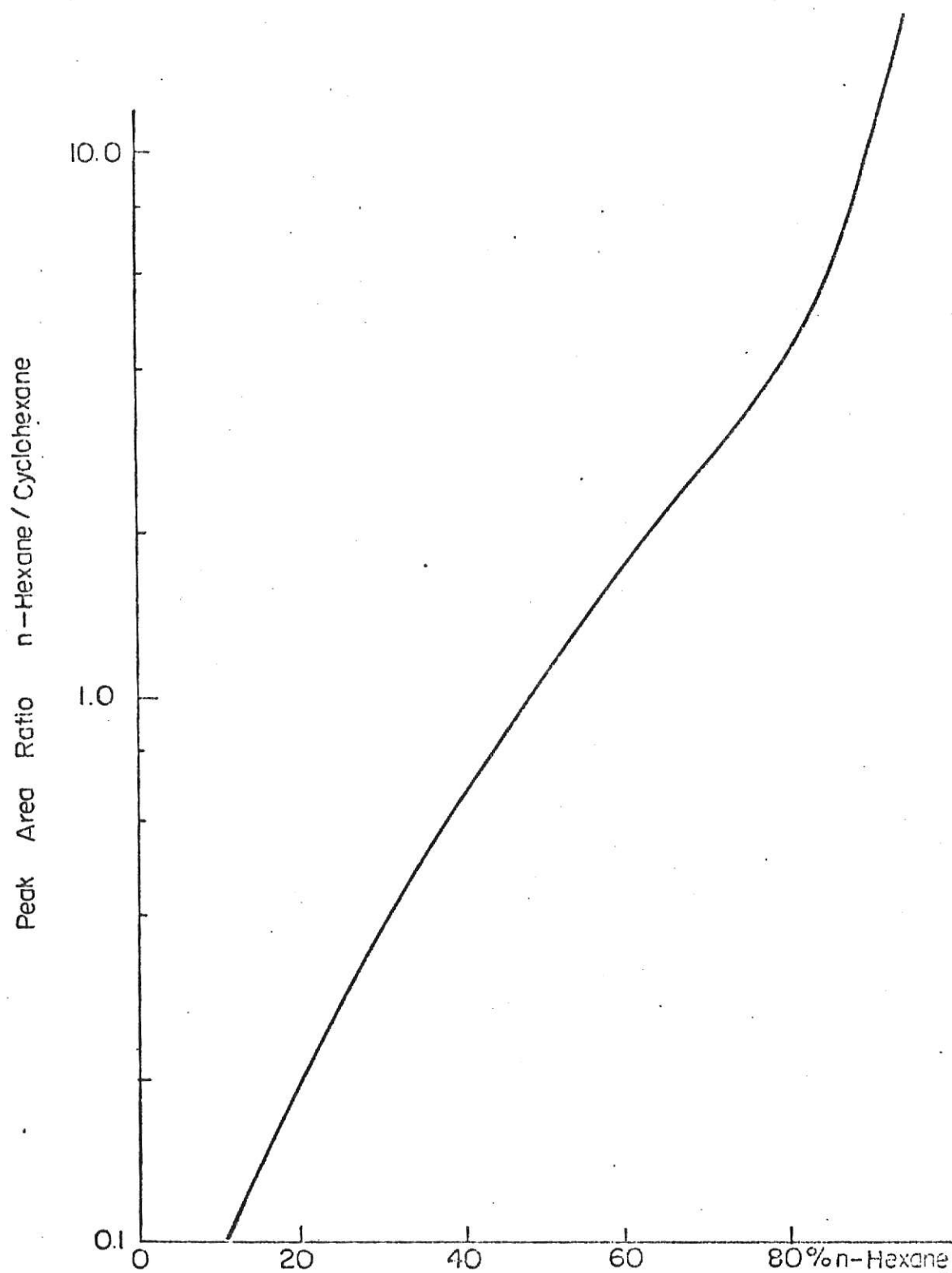
Fig. 10. Gas Chromatograph Calibration Curve for
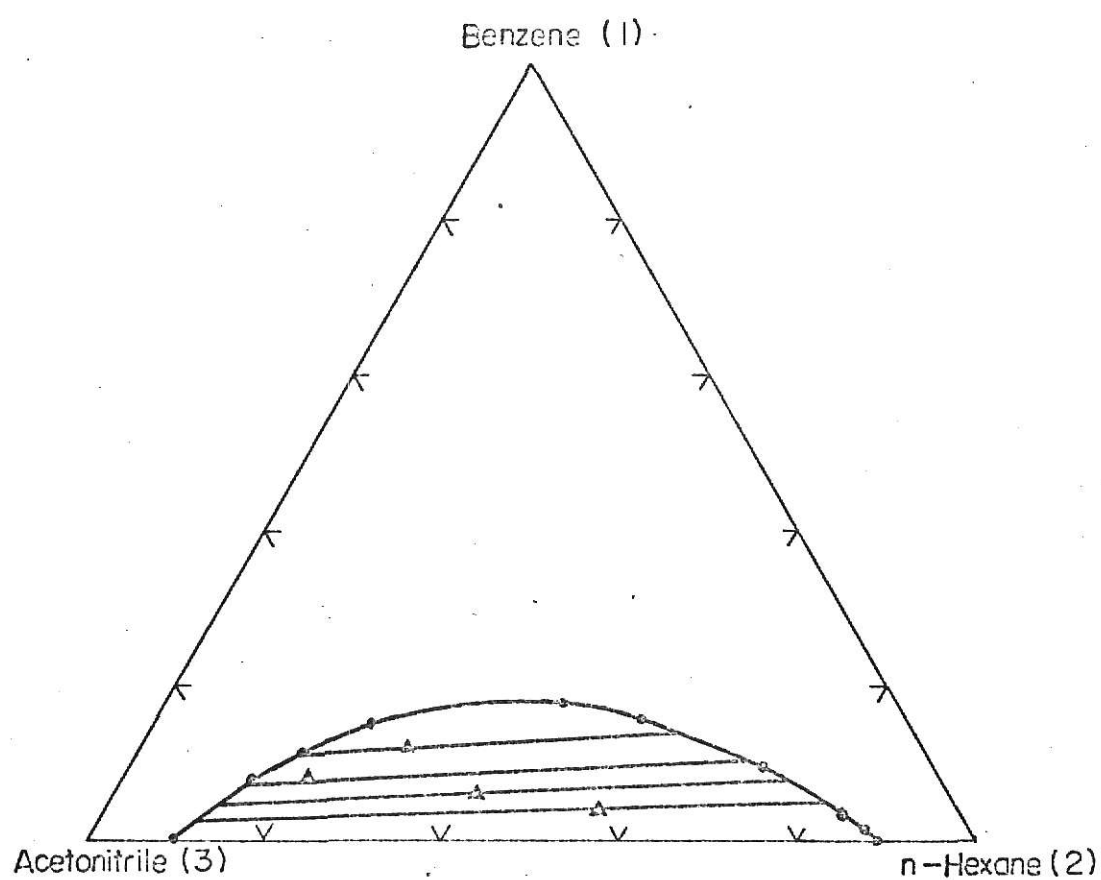n – Hexane ––– Cyclohexane system .

Fig. II.   Binodal   curve   and   tie   lines   for   the
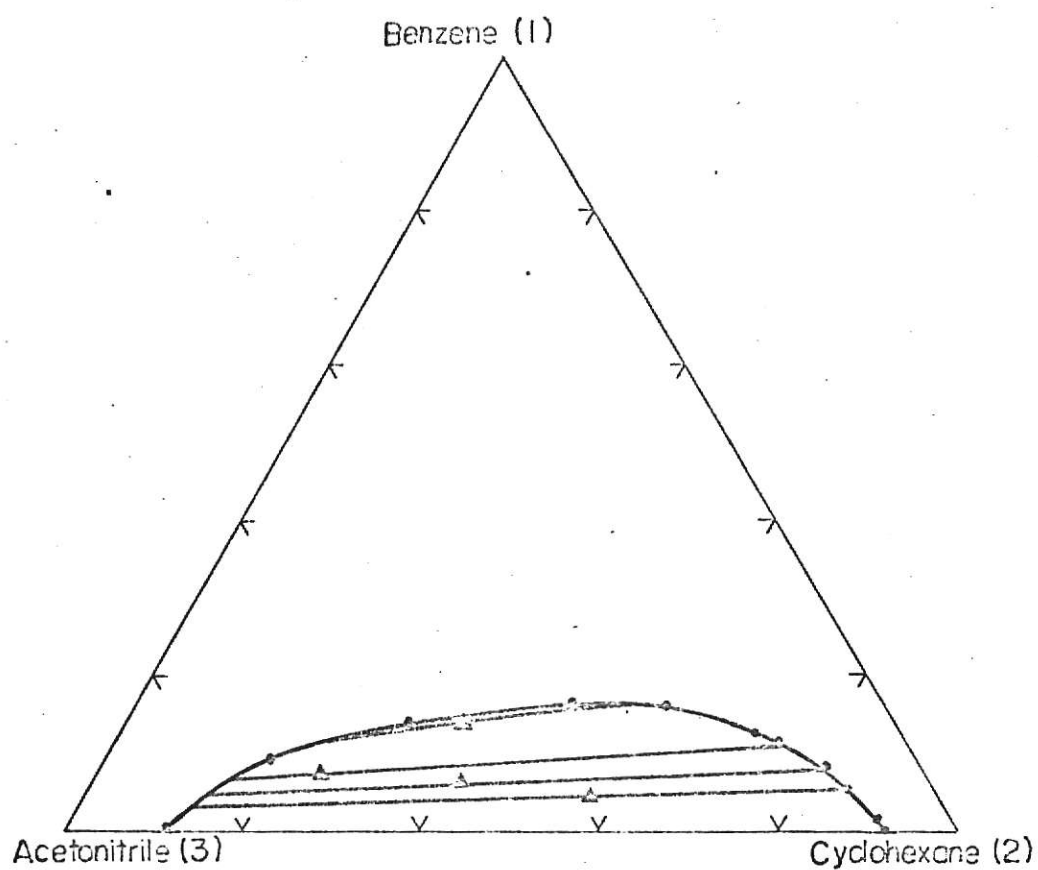system : Benzene (I) -- n-Hexane (2)--
Acetonitrile (3).

Fig. 12. Binodal curve and tie lines for system:
Benzene (1) -- Cyclohexane (2) -- Acetonitrile (3).
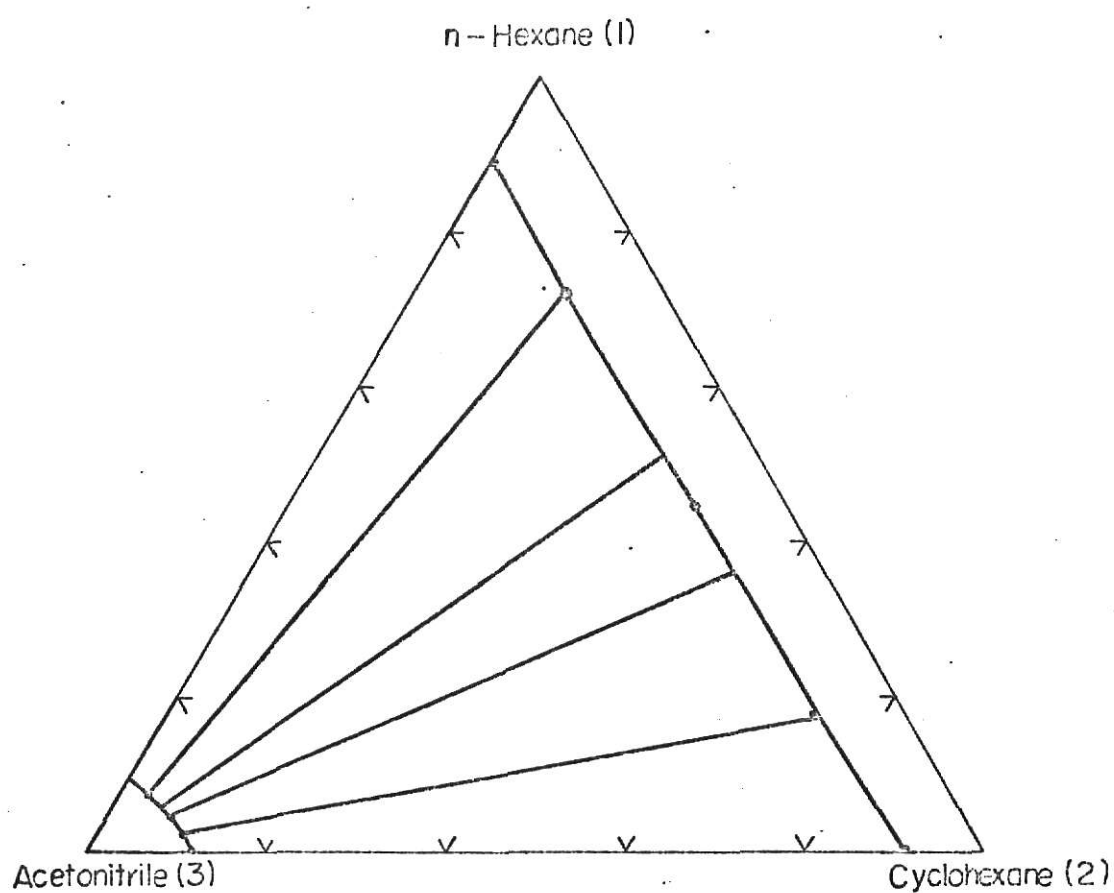
Fig. 13. Binodal curves and tie lines for the system : n-Hexane (1) -- Cyclohexane (2) -- Acetonitrile (3).
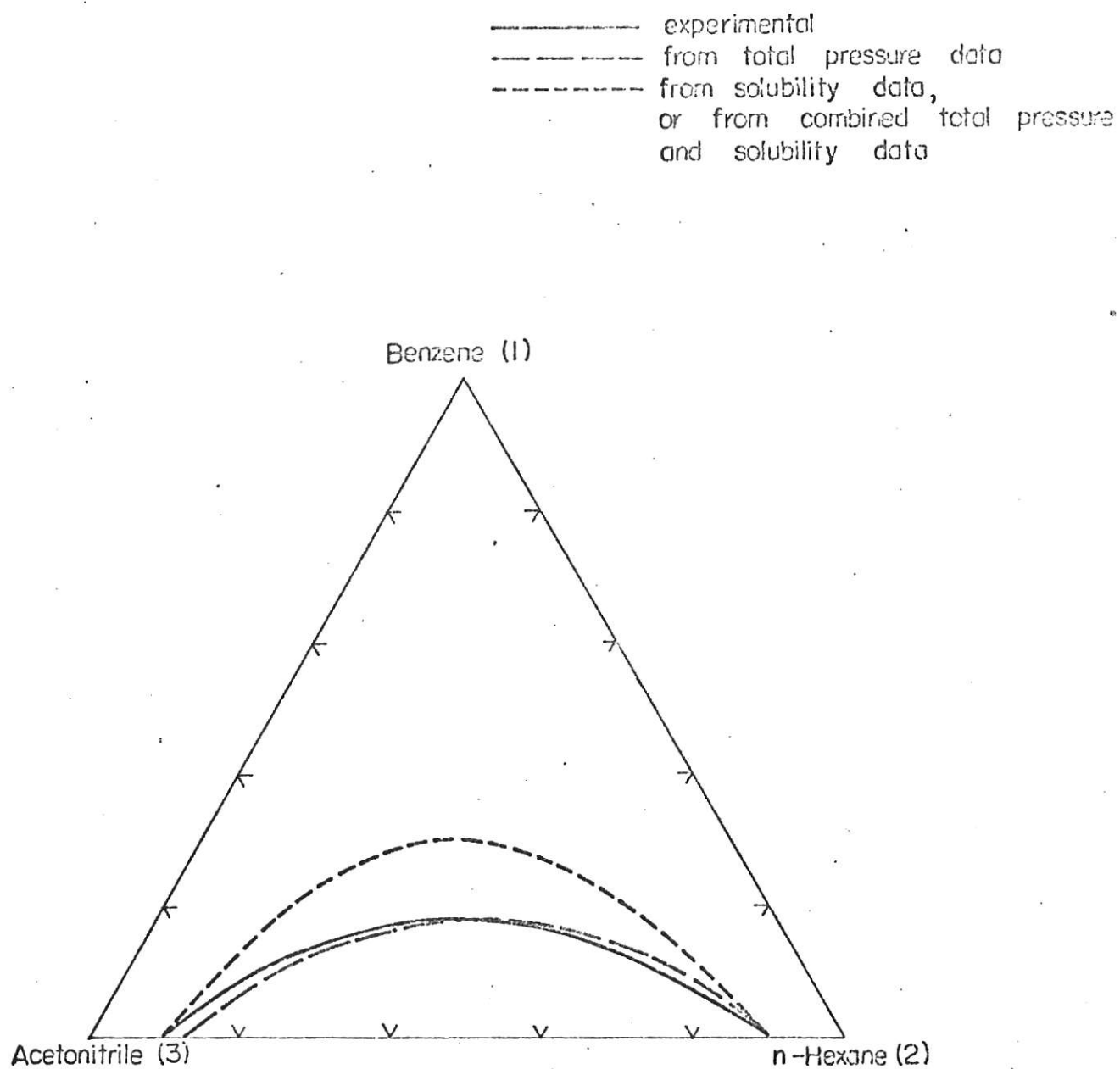
Fig.14. Comparison of Predicted and Experimental
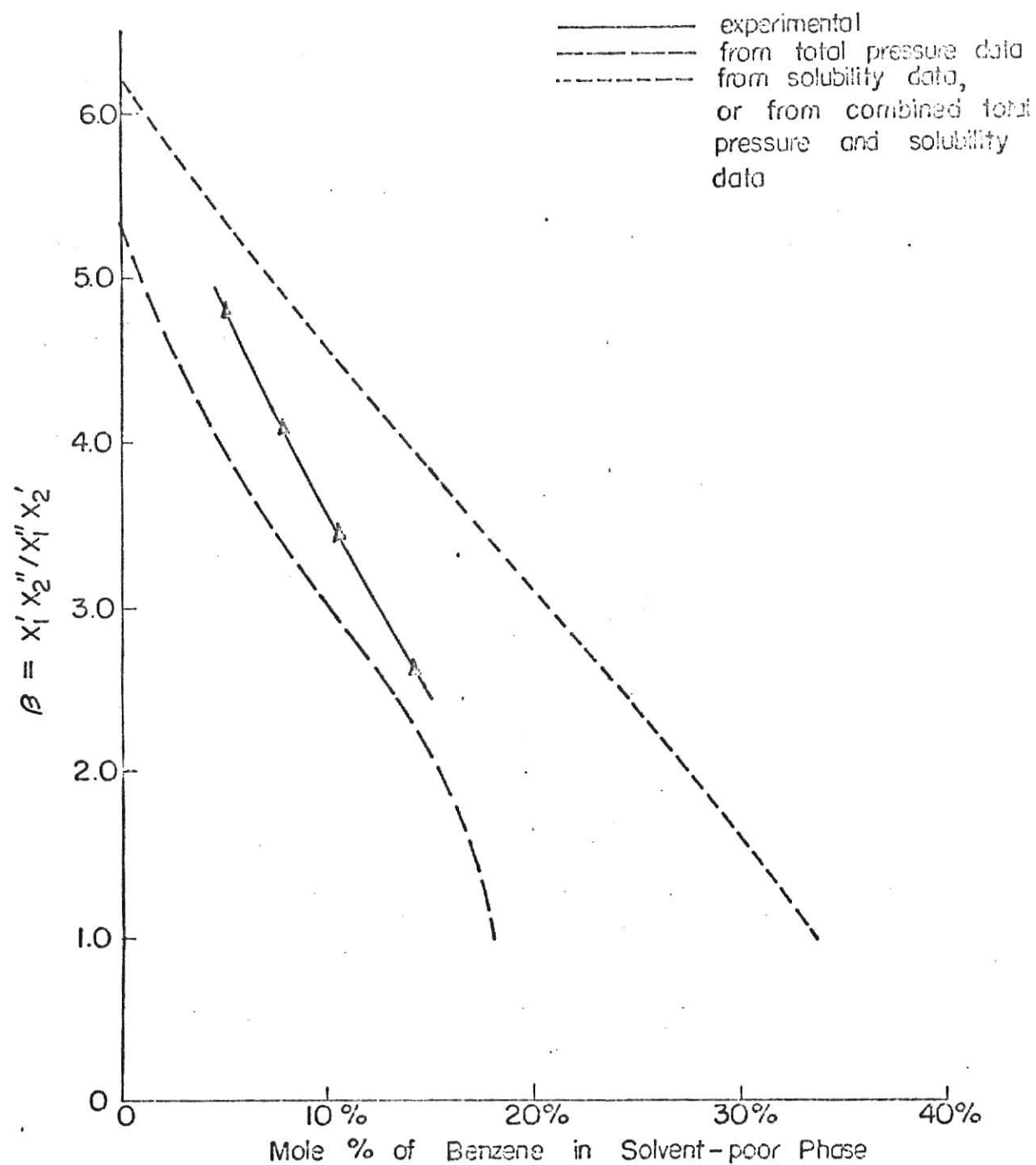Binodal Curve for the system: Benzene (I)
-- n—Hexane (2)-- Acetonitrile (3).

Fig. 15. Comparison of predicted and experimental solvent selectivity for the system : Benzene (1) —— n-Hexane (2) ——Acetonitrile (3) system.
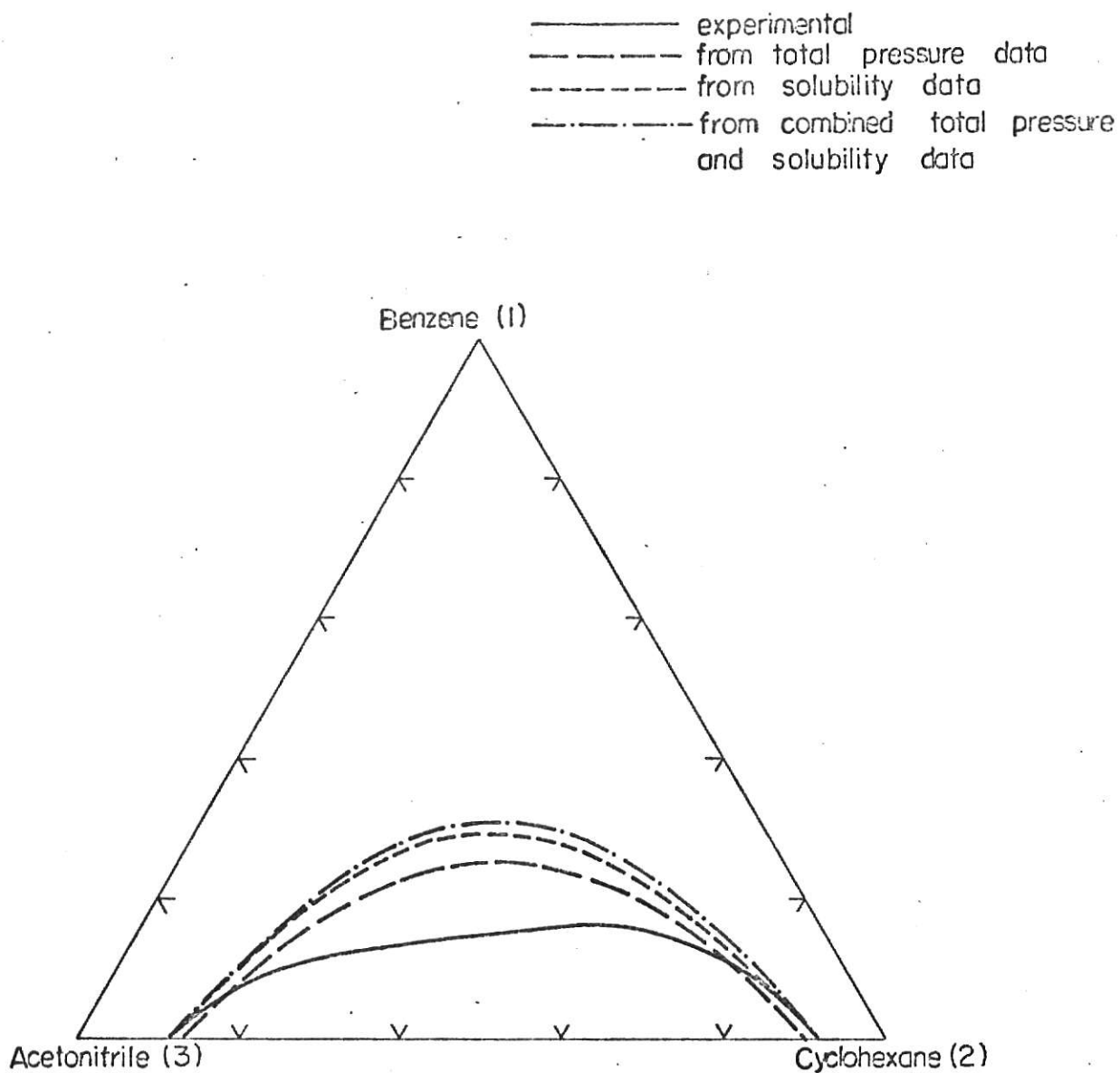
Benzene (1)

Acetonitrile (3)

Cyclohexane (2)

Fig. 16. Comparison of predicted and Experimental Binodal Curve for the system : Benzene (1) -- Cyclohexane (2) -- Acetonitrile (3).
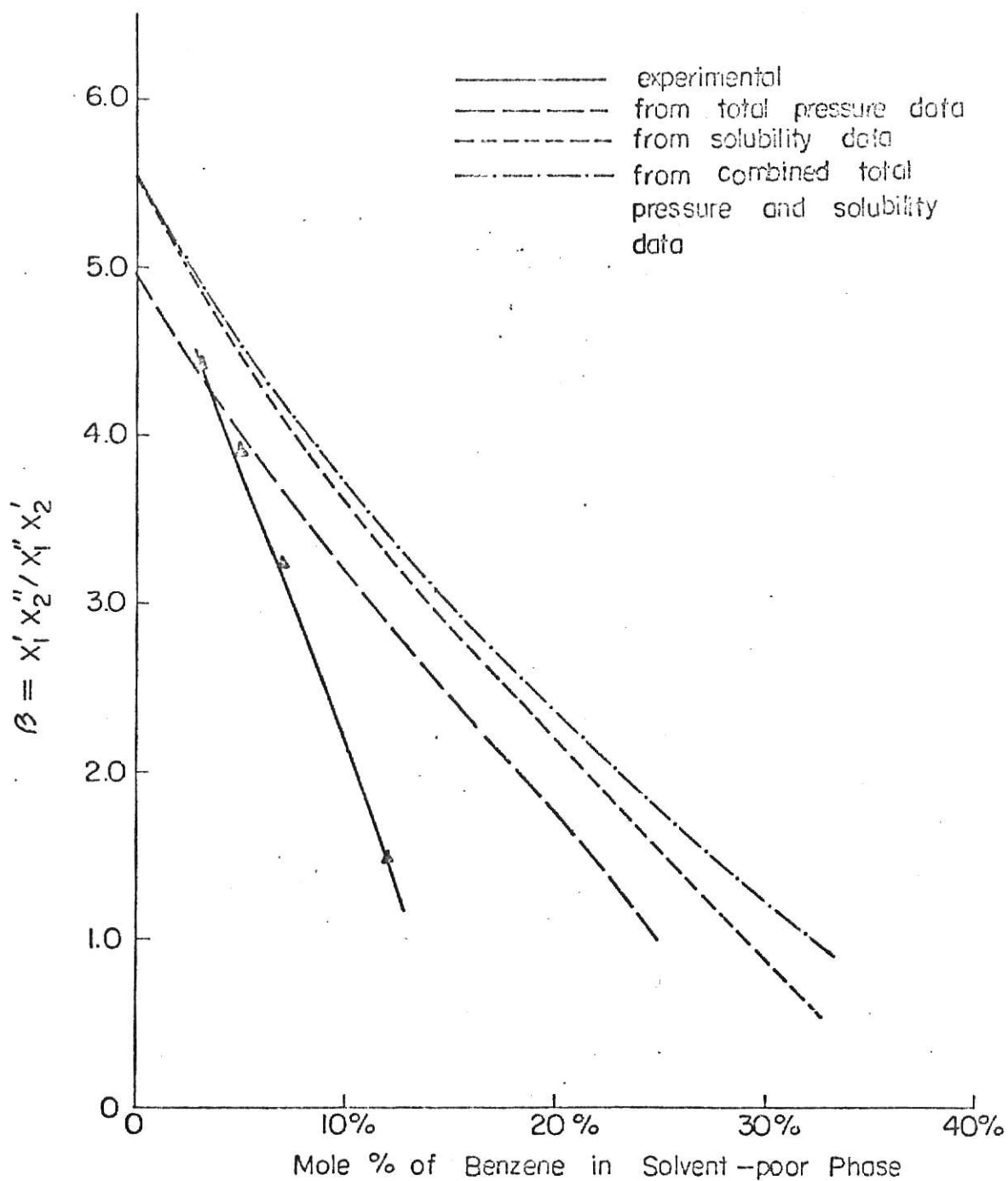
Fig. 17. Comparison of Predicted and Experimental Solvent Selectivity for the system : Benzene (1) — Cyclohexane (2) — Acetonitrile (3).

left hand curve :

—————— experimental,
or from solubility data,
or from combined total
pressure and solubility data
—————— from total pressure data

right hand curve :

—————— experimental
—————— from solubility data,
or from total pressure
data, or from combined
total pressure and
solubility data
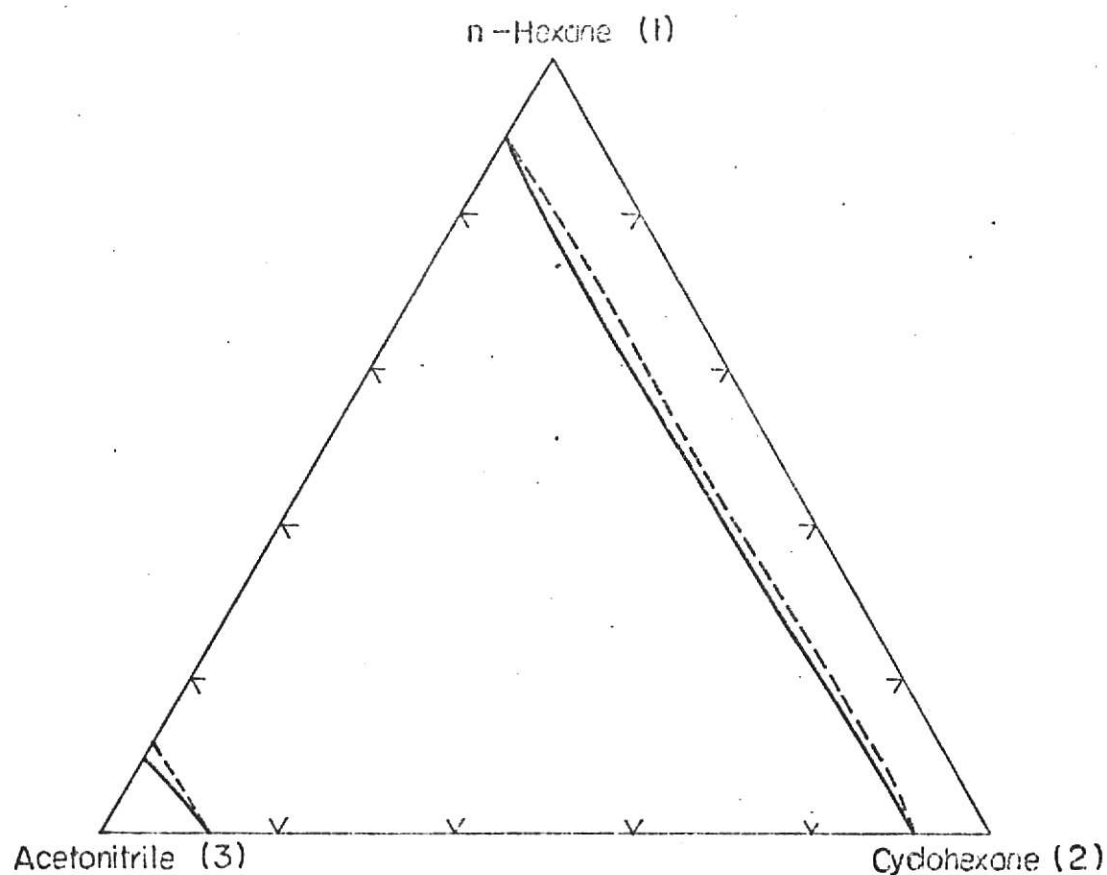

n —Hexane (1)

Acetonitrile (3)

Cyclohexane (2)

Fig. 18. Comparison of Predicted and Experimental Binodal curve for the system : n— Hexane (1) ——Cyclohexane (2) —— Acetonitrile (3)
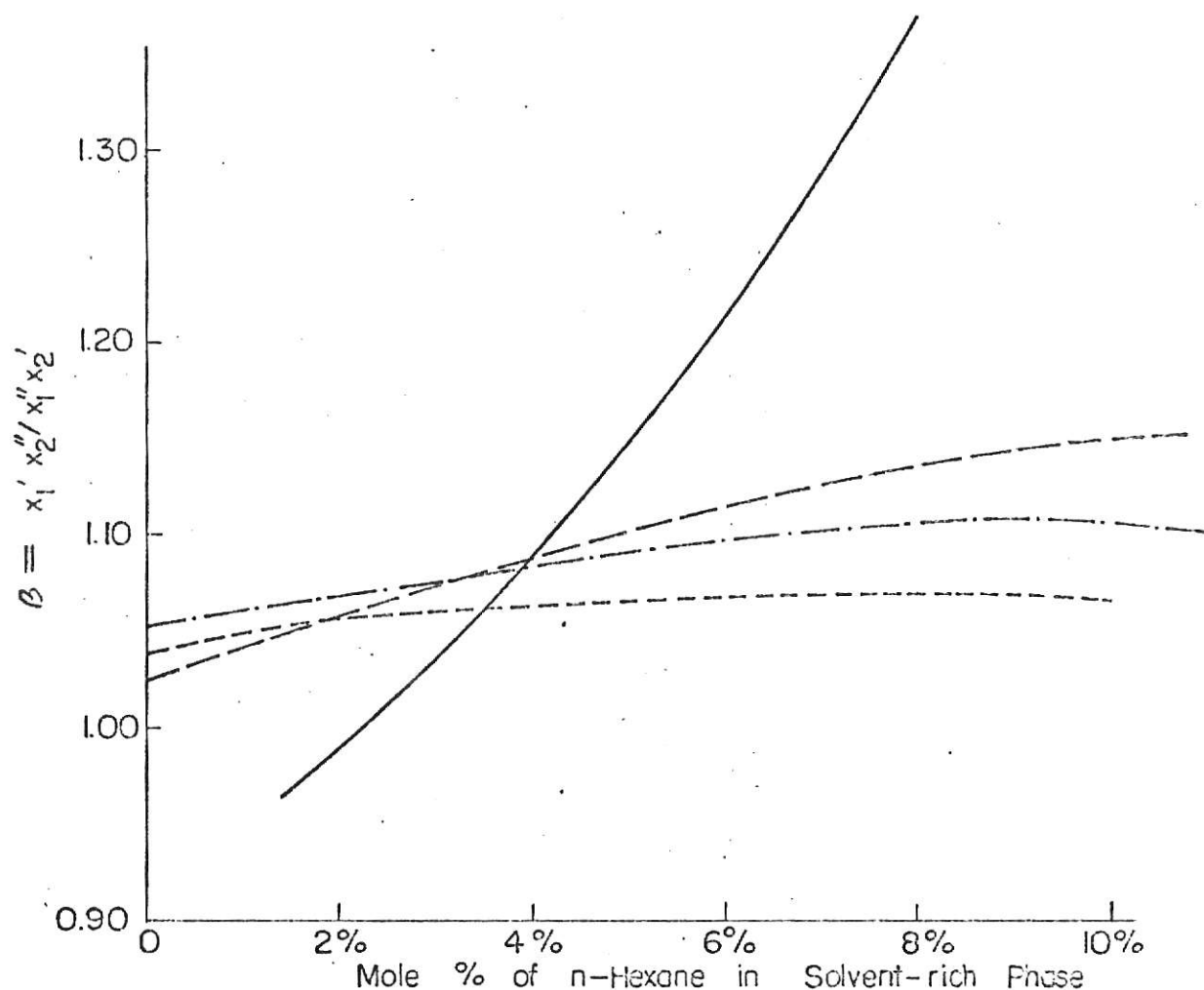
Fig. 19. Comparison of Predicted and Experimental Solvent Selectivity for the system : n—Hexane(1) —— Cyclohexane (2)——— Acetonitrile (3) system.

——————— experimental
—— —— —— from total pressure data
——————— from solubility data
——·——·—— from combined total pressure and solubility data

PHASE EQUILIBRIA IN
PARTIALLY MISCIBLE SYSTEMS

by

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B.S., National Taiwan University, 1967

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1970

Ternary liquid-liquid equilibrium data were obtained experimentally at 45° C for the following three systems: Benzene--n-Hexane--Acetonitrile, Benzene--Cyclohexane--Acetonitrile, and n-Hexane--Cyclohexane--Acetonitrile. Because gas chromatographic analysis showed only one reproducable quantitative analysis could be obtained for the ratio of two of the components in the ternary mixtures, it was necessary to first determine the binodal curve and then locate tie lines by determining the ratio of these two components in each of the coexisting liquid phases.

To test the feasibility of predicting ternary liquid-liquid equilibrium data with only binary information, a recently published activity coefficient equation, the NRTL equation, was used to calculated the predicted tie lines with the IBM 360/50 computer. The binary NRTL parameters for completely miscible binary systems were estimated from binary vapor-liquid equilibrium data. The binary NRTL parameters for partially miscible binary systems were estimated either from total pressure data, from mutual solubility data or from a combination of both. The predicted results from total pressure data were found always superior to the results from other data. Reasonably good predictions were obtained for all three systems. The deviations on a solvent-free basis were found to be comparable to deviations reported for prediction of ternary vapor-liquid equilibria.