

THERMODYNAMICS OF  
ACETONITRILE-HYDROCARBON SYSTEMS

by

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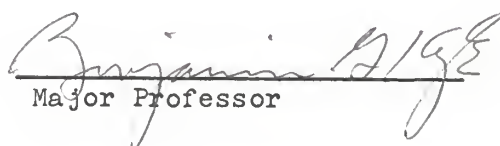
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## TABLE OF CONTENTS

I.	Introduction	1
II.	Experimental	
	2.1 Apparatus	3
	2.2 Operating Procedure	8
	2.3 Analysis	14
	2.4 Data	19
III.	Determination of Complete Vapor-Liquid Equilibrium Data of the Binary Systems from Total Pressure-Liquid Composition Measurements	
	3.1 Theoretical Background	22
	3.2 Calculation and Results	24
IV.	Discussion and Conclusions	42
	Acknowledgment	44
	Nomenclature	45
	Bibliography	46

## I. INTRODUCTION

One of the major problems facing chemical engineers involves the correlation, extension, and prediction of phase equilibrium data. Except for systems exhibiting ideal liquid phase behavior, this problem involves an understanding of the manner in which activity coefficients vary with composition (and temperature) in binary and multicomponent systems.

Prausnitz and coworkers [1] have presented ample evidence to show that activity coefficients in systems which deviate only moderately from ideal behavior can be well-represented by the Wilson equation [2]. These workers further showed that multicomponent vapor-liquid equilibrium data calculated by means of the Wilson equation with constants determined from binary data were in agreement with experimental measurements.

Two problems arise when considering partially miscible systems: (1) Deviations from ideal behavior are so large that it is difficult to fit activity coefficient data to an analytical expression of moderate complexity, (2) Sufficient reliable equilibrium data for partially miscible systems are not available so that the behavior of these systems can be characterized.

Renon [3] has attacked the first problem by deriving a semi-theoretical equation based on Scott's two-liquid model and a nonrandom mixture. This equation, referred to as the NRTL (nonrandom, two-liquid) equation, was shown to be capable of representing activity coefficients in systems exhibiting large positive deviations from ideal behavior when tested against

the few available experimental data.

The problem of insufficient experimental data for partially miscible systems has received little attention although these systems are of considerable practical interest. Probably the major reason for the neglect of these systems is the experimental difficulties encountered.

The goals of this study were: (1) to develop apparatus and experimental techniques for studying these difficult systems and (2) to obtain experimental data so that the behavior of partially miscible systems may be better characterized.

Systems composed of Acetonitrile, n-Hexane and Cyclohexane were chosen for study because there is a relatively large degree of mutual solubility and because the relatively high volatility of the components is advantageous for the equilibrium measurements. Isothermal vapor-liquid equilibrium data (including the two-liquid phase region) were determined for the n-hexane--acetonitrile system and the cyclohexane--acetonitrile system.

## II. EXPERIMENTAL

### 2.1 Apparatus

The equilibrium total vapor pressure measurements were conducted by the static method. The schematic arrangement of the apparatus is shown in Figure 2-1. The apparatus consisted of a thermostat containing an equilibrium cell (1), a differential pressure transducer (2) and a thermometer (3), an absolute pressure gauge (4), a differential pressure transducer indicator (5), a pressure regulating bellows (6) and a vacuum system.

Thermostat: The thermostat was an insulated 16"x16"x38" box. On the front side of the box there was a 10"x26" acrylic plastic pane which could be removed for servicing the equilibrium cell during shut-down. During a normal run, operation of the valves and stopcocks located inside the thermostat were done by hand through the isolating gloves hanging on the side walls of the box.

A 6" diameter fan circulated the air upward along the center and downward along the side of the thermostat. Around the fan were two nichrome heaters, one of them was regulated manually by a rheostat and the other was automatically controlled by a Thermistep Model 63 Temperature Controller. The temperature variation of the thermostat was less than  $\pm 0.01^{\circ}$  C. while maintained at  $45^{\circ}$  C., and was almost at a uniform temperature throughout the system.

Equilibrium Cell: The equilibrium cell was as shown in Figure 2-2. It was constructed of two major parts -- the vapor sample

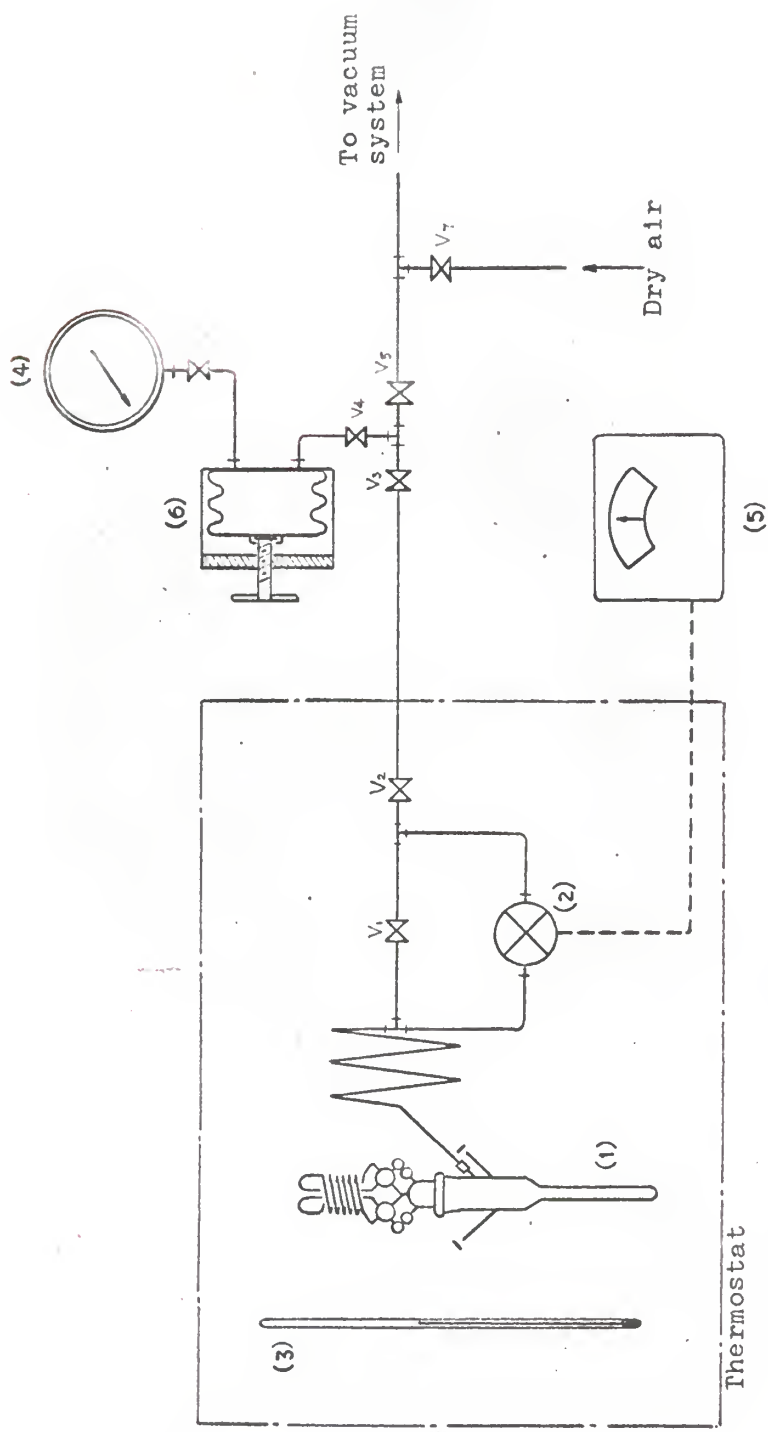


Fig. 2-1. Schematic arrangement of apparatus.

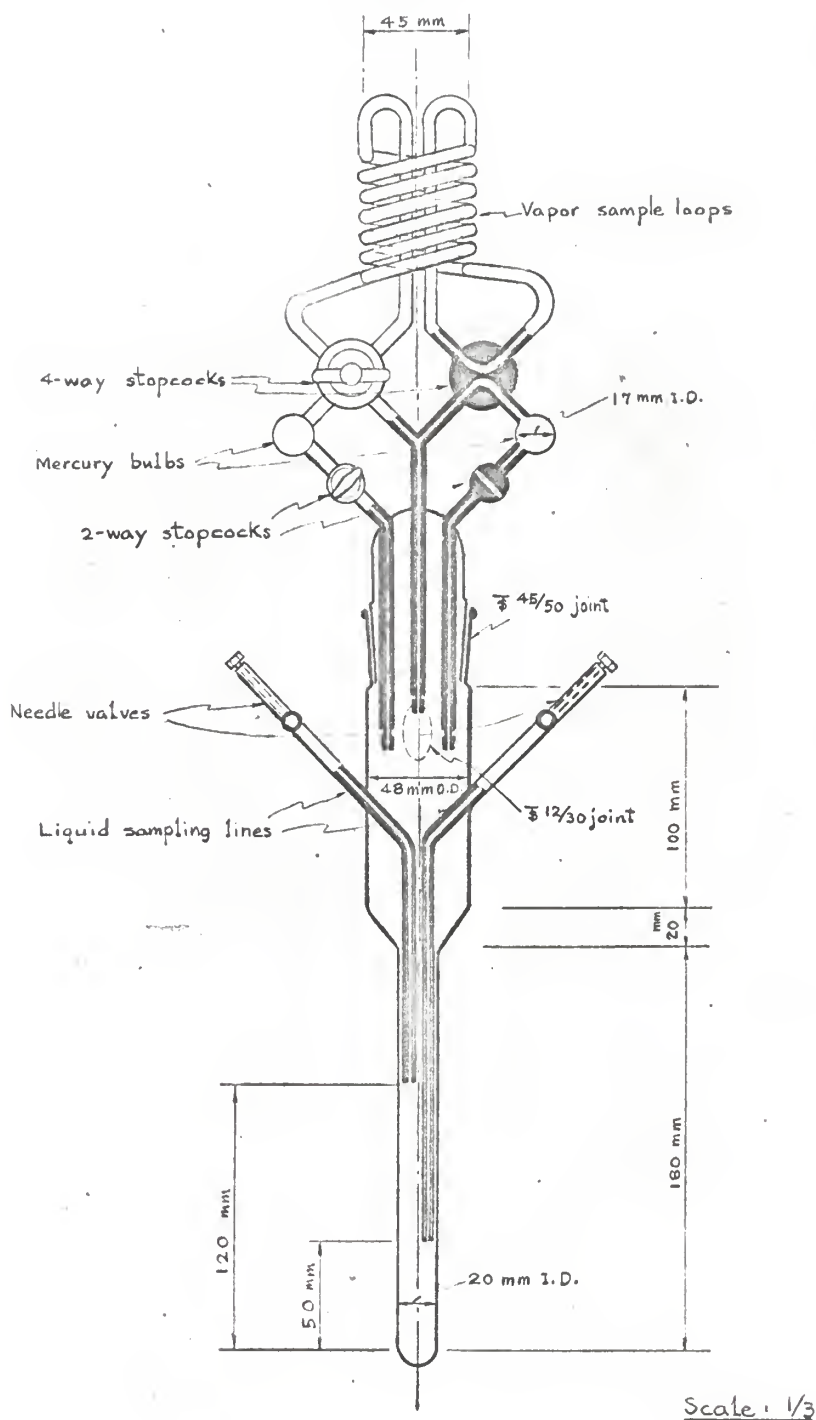


Fig. 2-2. Equilibrium Cell.

collector and the equilibrium chamber, and was made of Pyrex glass. The vapor sample collector consisted of two sample loops each made from 4 feet of size C capillary tubing and sealed to a four-way, twin-V bore stopcock. The loops were wound together into the form of a coil. An insulated nichrome wire was wound around the sample loops so that the loops could be heated by passing an electric current through the wire.

The cell was connected through a  $\frac{1}{2}$  12/30 ground-glass-metal joint to the differential pressure transducer by 1/8" O.D. copper tubing. In the equilibrium chamber, there were two liquid sampling tubes made of size C capillary tubing. These liquid sampling tubes were closed by Fischer & Porter Lab-Crest  $1\frac{1}{4}$  mm needle valves and terminated in female Luer joints.

The vapor sample collector and the equilibrium chamber were coupled together by a  $\frac{1}{2}$  45/50 ground-glass joint. When the determination of vapor composition was not required, the vapor sample collector was replaced by a cap.

The equilibrium cell was mounted on a shaker driven by a motor located on the top of the box. A sketch of the shaker mechanism is shown in Figure 2-3. The speed of the motor was regulated by a Gerald K. Heller Co.'s Model SX10A Motor Controller.

Temperature Measurement: A Fisher Cat. No. 15-o43 glass thermometer with  $0.1^{\circ}$  C. subdivisions was used to measure temperature. The thermometer was crosschecked with several other similar thermometers and the error at  $45^{\circ}$  C. was estimated to be less than  $\pm 0.05^{\circ}$  C.



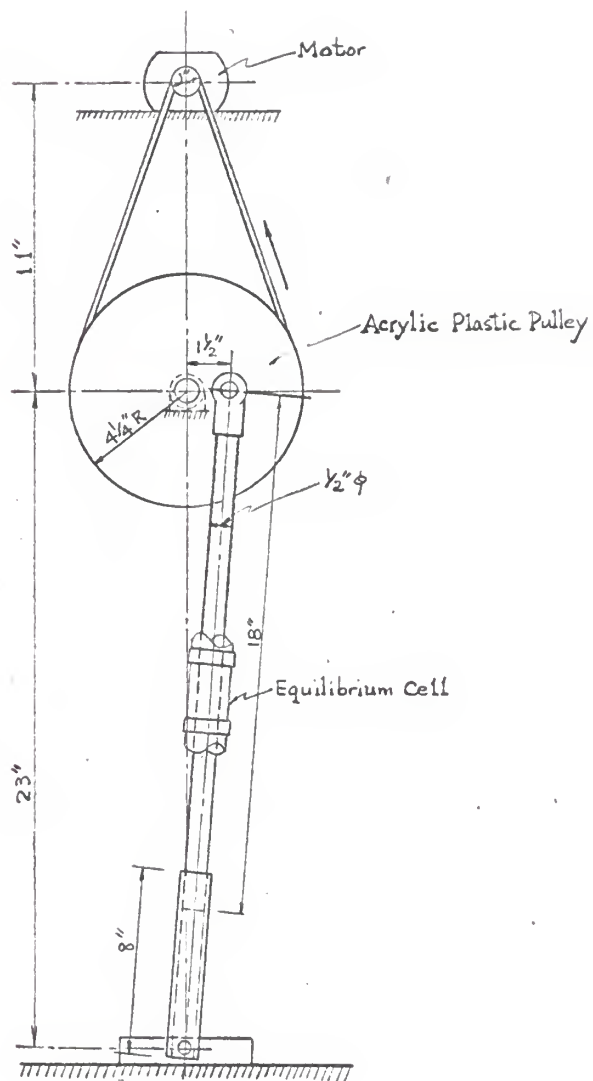


Fig. 2-3. Shaker of Equilibrium Cell.

Pressure Measurement: A pressure transducer and an indicator manufactured by Pace Engineering Company were used to detect the pressure difference between the equilibrium cell and the absolute pressure gauge. The sensitivity of the transducer was better than  $\pm 0.1$  mm Hg. With the transducer by-pass valve,  $V_1$ , closed, the air pressure in the absolute pressure gauge was adjusted by varying the volume of the pressure regulating bellows until the reading on the transducer indicator came to zero. With the transducer indicating zero pressure differential, the vapor pressure in the equilibrium cell could then be read indirectly from the pressure gauge. The absolute pressure gauge was a Wallace & Tiernan Model No. FA129, with 1 mm Hg subdivisions. The gauge had been calibrated against a mercury manometer-cathetometer system and required no correction.

Vacuum System: The vacuum pump was capable of pumping down to about 1 mm Hg absolute. A liquid nitrogen cooled vapor trap was placed ahead the pump.

## 2.2 Operating Procedure

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

Preparation of Equilibrium Cell: The vapor sample collector was filled with mercury before each run. The device used for

filling the collector with mercury is illustrated in Figure 2-4.

A syringe equipped with a two-way stopcock,  $V_1$ , was filled with mercury and placed on the terminal "a" of the vapor sample collector. With the stopcocks turned to the positions as illustrated in Figure 2-4, the terminal " $b_1$ " of the collector was attached to a vacuum pump and one half of the apparatus, including one sample loop, was evacuated. Then  $V_2$  was closed  $V_1$  opened, and the mercury was introduced into the loop via the syringe. The procedure was repeated to fill the other half of the apparatus with mercury. After the entire apparatus was filled with mercury, the syringe was removed and the vacuum pump was disconnected. With the four-way stopcocks remaining in the position of  $V_3$  in Figure 2-4, the mercury in the apparatus was warmed up to a temperature above  $45^\circ \text{C}$ . and then the four-way stopcocks were rotated to seal off the sample loops while the mercury was warm.

Before charging the specimen solution into the equilibrium cell, the liquid sampling tubes were completely purged with dry air to assure that no solution of the previous run remained in the tubes. If the specimen solution was a two-liquid phase mixture, about 50 ml of the solution would be charged, and if it was a single phase mixture, about 30 ml of the solution would be charged. The vapor sample collector and the equilibrium chamber were coupled together and the joint was further sealed by applying a coat of Fisher Sealit over the seam of the joint.

Derassing: After the apparatus had been assembled, the foreign gases present in the vapor space as well as dissolved in the

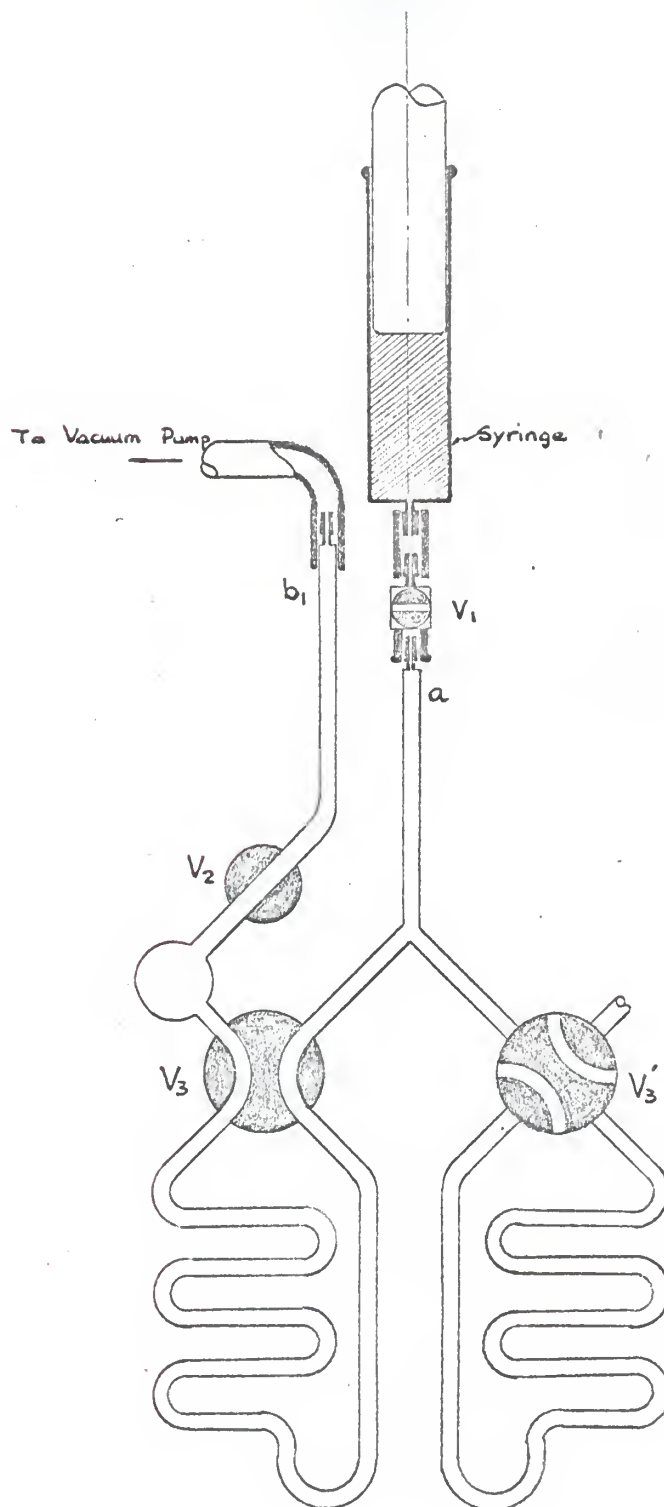


Fig. 2-4. Device for filling Vapor Sample Collector with mercury.

specimen solution were removed from the equilibrium cell. This was accomplished by freezing the specimen solution with liquid nitrogen until it had become solid, then evacuating the cell through the vacuum system. During the evacuation, the transducer by-pass valve,  $V_1$ , and valve  $V_2$  in Figure 2-1 were open. After the evacuation of the cell was complete, valve  $V_2$  was closed and the frozen specimen solution allowed to melt. When this process was repeated three times, the equilibrium cell together with the specimen solution was effectively degassed, and no bubble formation during normal freezing was observed. Before evacuating the system, care was exercised to assure that the two-way stopcocks on the vapor sample collector were closed. The melting of the frozen specimen was accelerated with the aid of a portable hot air blower. At the end of the degassing process the transducer by-pass valve,  $V_1$ , was closed instead of valve  $V_2$ , and the four-way stopcocks of the vapor sample collector were turned to seal off both the sample loops and the mercury bulbs.

Determination of Equilibrium and Collections of Samples: After the temperature of the thermostat had been brought to  $45^{\circ}\text{C}$ ., the equilibrium cell was then shaken frequently to agitate its contents. In the mean time the air pressure in the absolute pressure gauge was adjusted so as to maintain the pressure difference between the equilibrium cell and the absolute pressure gauge at a minimum until no further change in vapor pressure in the equilibrium cell was observed, then the transducer indicator was adjusted to zero and the equilibrium total vapor pressure of the mixture was determined.

Before introducing vapor samples into the sample loops, the sample inlet tubes were purged by dropping out about 2/3 of the mercury stored in the mercury bulbs with the four-way stopcocks turned to the position of  $V_1$  in Figure 2-8(A) and by opening the two-way stopcocks. After the sample inlet tubes had been purged, the four-way stopcocks were turned to the position of  $V_1$  in Figure 2-8(B), then the vapor sample was introduced into the sample loops while the mercury in the loops dropped out. After the vapor sample had been collected, the four-way stopcocks were then rotated to seal off the sample loops.

For collecting liquid samples, the equilibrium cell was first pressurized to about 10 to 20 mm Hg above the atmospheric pressure by introducing dry air from outside, then the liquid samples were pushed out of the cell through the liquid sampling tubes and introduced into 1/16" O.D. indium tubing attached to the sampling terminals as shown in Figure 2-5. The liquid samples were then sealed into the indium tube capsules of about 5 mm long, using a special crimping tool manufactured by Sargent & Company. Usually 10 to 15 capsules for each liquid sample were prepared for analysis.

During the collection of samples, the temperature of the thermostat was maintained at  $45^{\circ}$  C. Before the vapor sample collector was removed from the thermostat for analysis, the sample loops were warmed up to above  $45^{\circ}$  C. and were kept warm during the analysis to prevent vapor condensation.

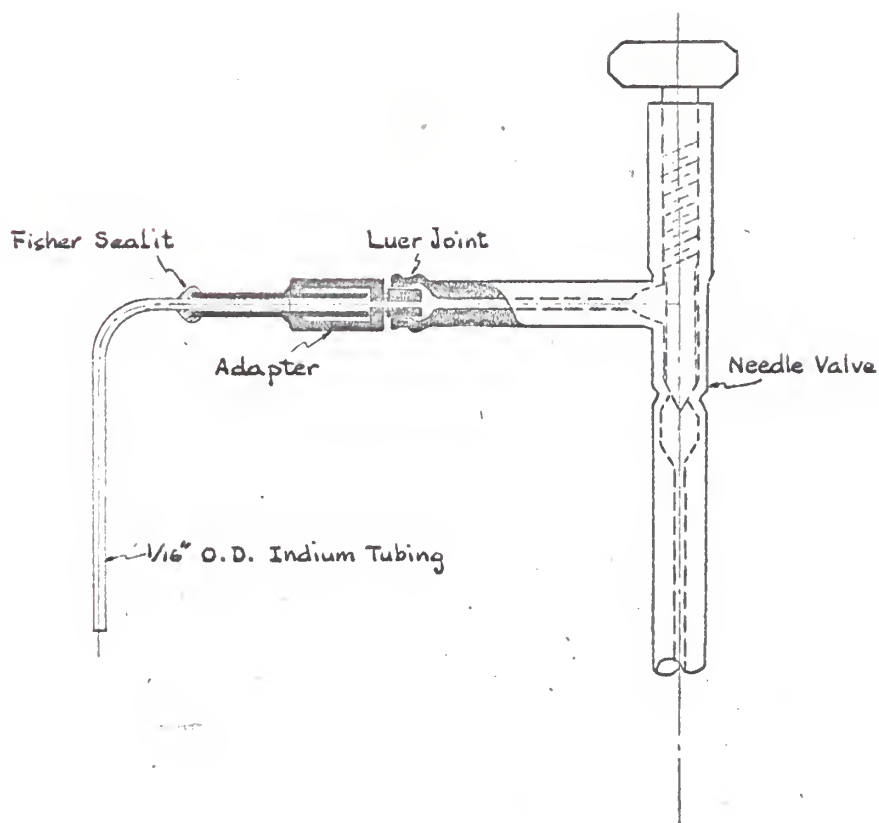


Fig. 2-5. Collection of liquid samples.

### 2.3 Analysis

The vapor and liquid samples were analyzed chromatographically to determine their compositions. A Varian Aerograph Model 600 D Gas Chromatograph, associated with a Sargent Model SR Recorder and a Disc Integrator Model 204, was used for the analysis.

The chromatographic column was a 5 ft.x1/8 in. O.D. stainless steel tube packed with 20% DEGS on 60/80 Chrom W supplied by the Varian Aerograph Company. The detector was a flame ionization detector, and nitrogen was the carrier gas. The temperature of the column was maintained at 60° C. and the liquid sample size was approximately 1 microliter.

The ratios of the chromatogram peak areas for n-hexane and acetonitrile as well as cyclohexane and acetonitrile were found to be sensitive to changes in liquid sample size, especially when the sample sizes were smaller than 0.8 microliter, however, no significant effect was observed if sample sizes were within the range of 0.8 to 1.5 microliters.

The correction factors which converted the area ratios of the chromatographic peaks to the weight ratios of the components for n-hexane--acetonitrile and cyclohexane--acetonitrile systems were found to vary with the composition of the mixture. Calibration curves for both systems were constructed by use of liquid mixtures of known composition prepared by weighing. To the partially miscible mixtures, benzene was added as a solvent so as to convert the mixtures into single phases. The calibration curves



are shown in Figures 2-6 and 2-7. The standard relative deviation,  $\sigma_{rel.}$ , of the chromatographic peak area ratios was normally about 3 to 3.5%. Therefore, an arithmetic average was taken of 8 to 10 measurements to determine a correction factor or a composition.

To introduce the vapor sample into the chromatograph, the terminals "a" and "b<sub>1</sub>" of the vapor sample collector as shown in Figure 2-8 were tied into the carrier gas stream with Teflon tubing. With the stopcocks in the positions shown in Figure 2-8(A), carrier gas was swept through b<sub>1</sub>c<sub>1</sub>a to purge the sample lines. The four-way stopcock V<sub>1</sub> was then momentarily turned to the position shown in Figure 2-8(B), and a plug of gas in the sample loop was swept onto the chromatographic column. The amount of the sample gas swept onto the column depended upon the length of time stopcock V<sub>1</sub> remained in the position shown in Figure 2-8(B). It was usually possible to obtain four or five measurements from one sample loop.

To introduce the liquid sample into the chromatograph, the indium capsule containing the liquid sample was melted in a furnace swept by carrier gas and the sample was released and vaporized. The apparatus used for introducing the liquid sample into the chromatograph was an Aerograph Inductor Model No. 695 manufactured by Wilkens Instrument and Research Inc. The temperature of the furnace was maintained at 350° C.

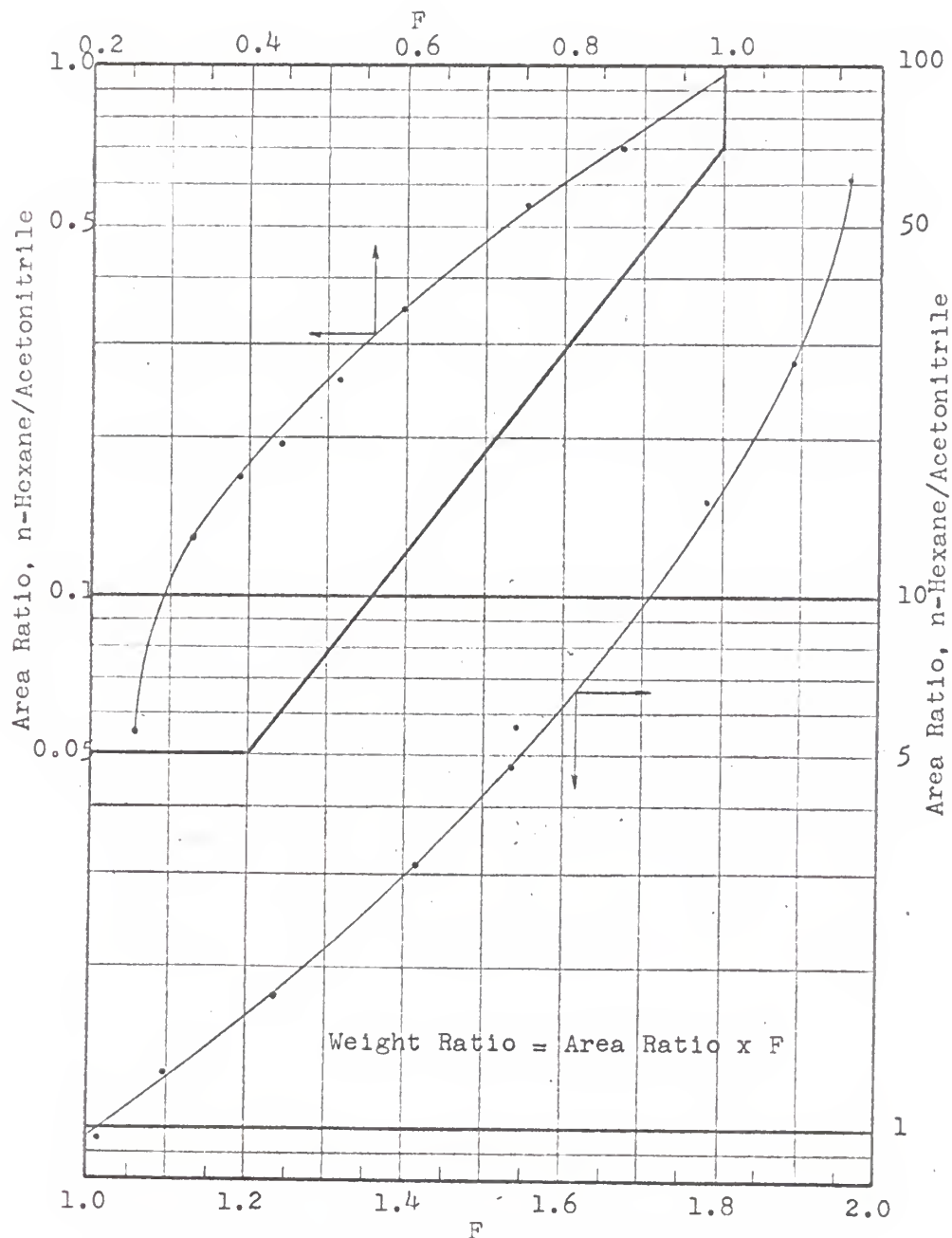


Fig. 2-6. Gas Chromatograph Calibration Curve  
 System: n-Hexane--Acetonitrile  
 Column: 5'x1/8" SS 20% DEGS on 60/80  
 Chrom W  
 Column Temperature: 60° C.  
 Sample Size: 1 microliter (liquid).

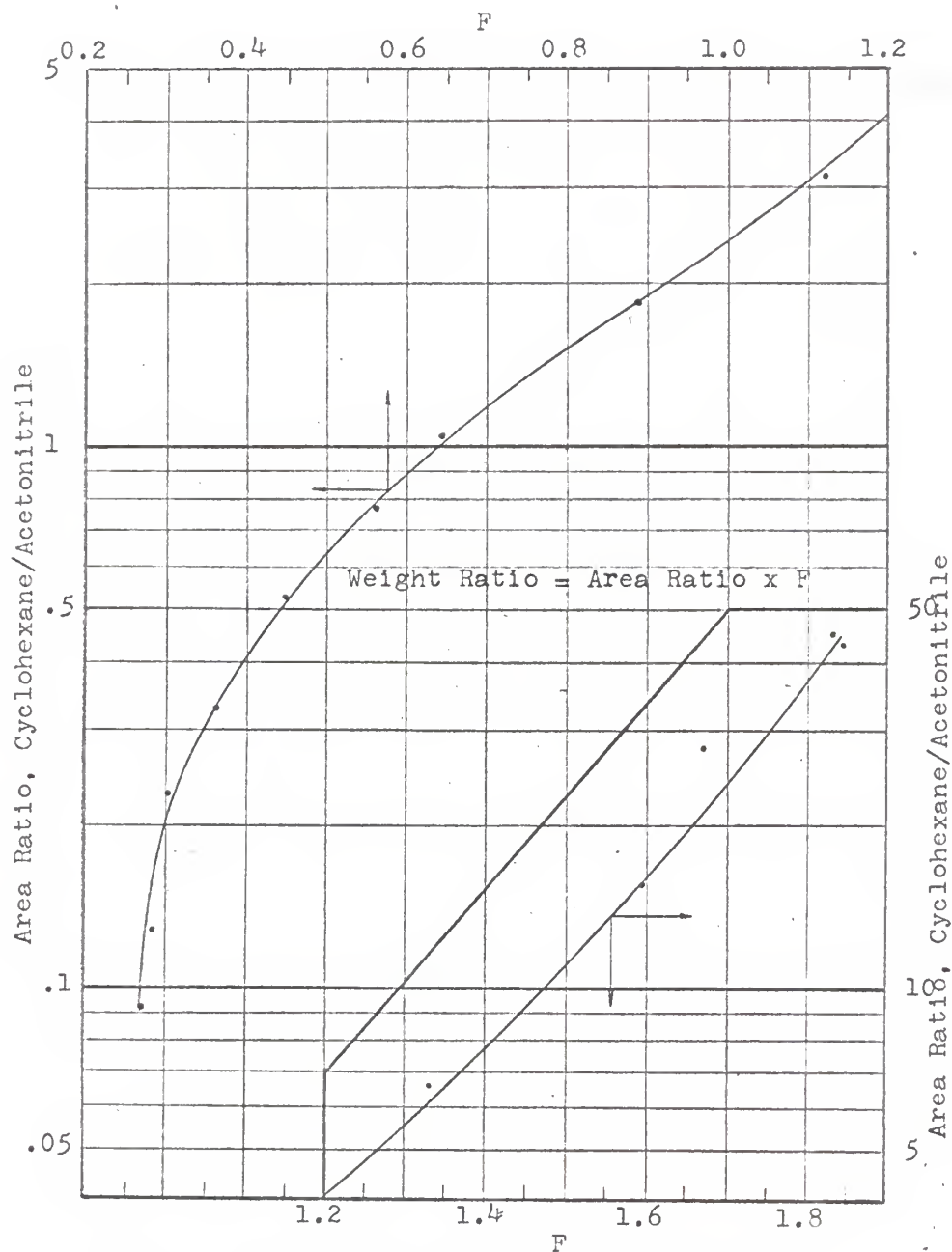


Fig. 2-7. Gas Chromatograph Calibration Curve  
 System: Cyclohexane--Acetonitrile  
 Column: 5'xl/8" SS 20% DEGS on 60/80  
 Chrom W  
 Column Temperature: 60° C.  
 Sample Size: 1 microliter (liquid).

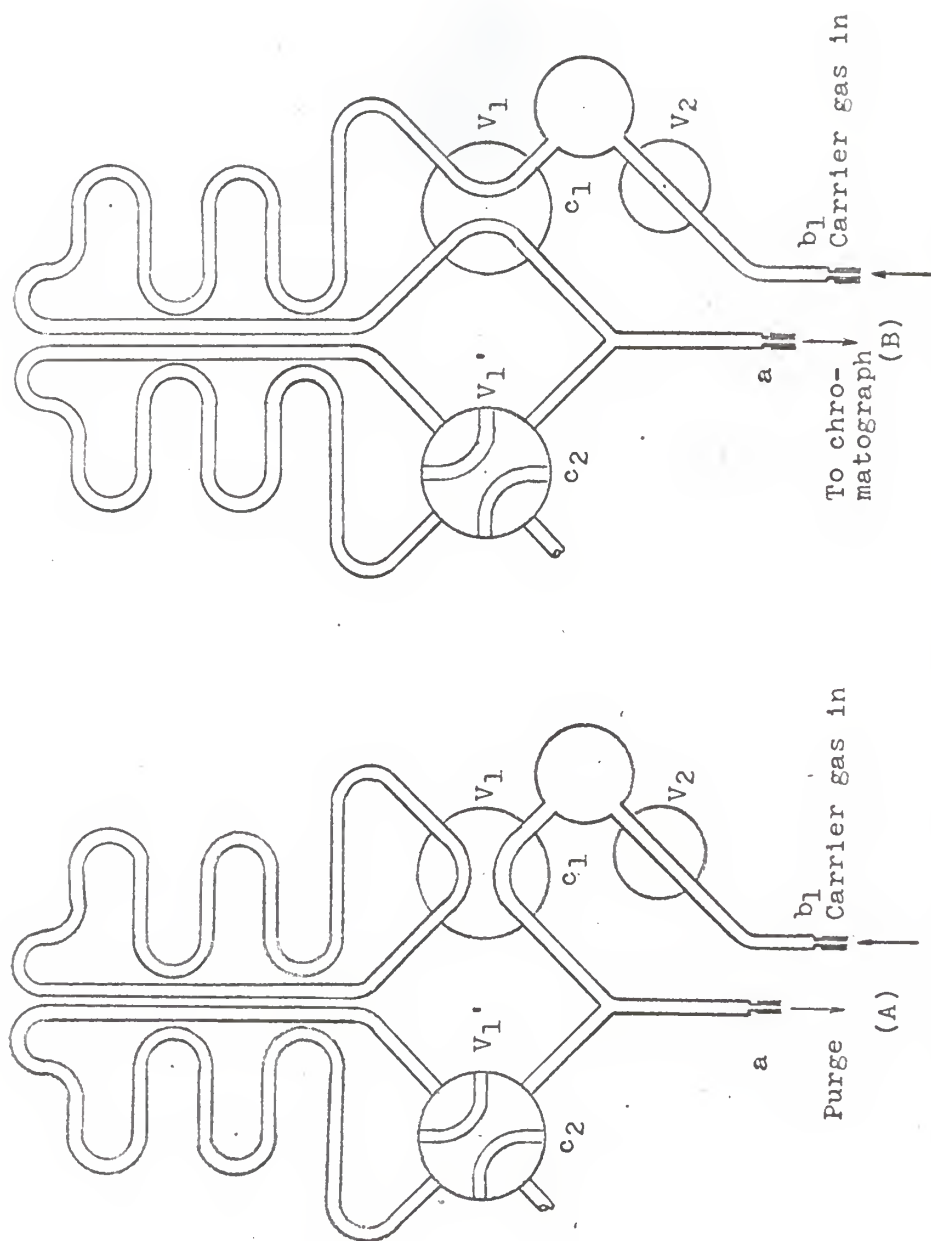


Fig. 2-8. Introduction of vapor sample into Chromatograph.

## 2.4 Data

The experimentally determined equilibrium total vapor pressure-liquid composition data are listed in Tables 2-1 and 2-2, and plotted in Figures 3-5(a),(b) and 3-6(a),(b).

For binary systems, vapor phase compositions can be calculated by rigorous thermodynamic equations from the total pressure-liquid composition data measured at a constant temperature and hence direct determination of vapor compositions is unnecessary. The apparatus and experimental techniques developed for determining multicomponent vapor compositions at low pressure were tested for their accuracy and precision on the n-hexane--acetonitrile system. These vapor composition data are also listed in Table 2-1, and will be compared with those calculated from the thermodynamic equations in Chapter 3.

Table 2-1. Total Vapor Pressure-Liquid Composition  
-Vapor Composition Measurements

System: n-Hexane--Acetonitrile at 45° C.

P mm Hg.abs.	x <sub>1</sub> Mole Fraction n-Hexane in Liquid	y <sub>1</sub> Mole Fraction n-Hexane in Vapor
213.0	0.0000	.000
291.2	0.0135	.312
300.3	0.0159	.386
314.2	0.0203	.419
357.0	0.0324	.455
381.4	0.0397	.487
403.2	0.0445	
407.2	0.0502	.492
420.1	0.0550	.507
443.2	0.0638	.567
459.0	0.0686	.584
462.0	0.0710	
482.1	0.0819	
493.0	0.0910	.598
500.8	0.0945	
520.5	0.121	
		.643
520.5	0.8525	
518.7	0.8780	
509.1	0.9154	
497.0	0.9305	
491.6	0.9416	
473.3	0.9539	
446.0	0.9706	
343.3	1.0000	

Table 2-2. Total Vapor Pressure-Liquid Composition Measurements

System: Cyclohexane--Acetonitrile at 45° C.

P mm Hg. Absolute	x <sub>1</sub> Mole Fraction Cyclohexane in Liquid
213.0	0.0000
239.0	0.0116
258.7	0.0190
269.1	0.0246
281.9	0.0296
295.4	0.0339
309.7	0.0411
323.4	0.0501
335.2	0.0536
345.3	0.0600
365.0	0.0715
374.8	0.0755
370.3	0.0760
390.0	0.0867
396.6	0.0990
406.3	0.106
408.5	0.112
409.0	0.120
409.0	0.8877
403.0	0.9081
395.0	0.9195
388.8	0.9271
377.3	0.9418
344.6	0.9644
328.0	0.9686
325.2	0.9793
233.7	1.0000

### III. DETERMINATION OF COMPLETE VAPOR-LIQUID EQUILIBRIUM DATA OF THE BINARY SYSTEMS FROM TOTAL PRESSURE-LIQUID COMPOSITION MEASUREMENTS

#### 3.1 Theoretical Background

Determination of vapor-liquid equilibrium data from total pressure-liquid composition measurements can be achieved either by (1) direct step-wise integration of the Gibbs-Duhem equation as illustrated by Othmer et. al. [4], or (2) evaluation of the constants of equations representing the liquid activity coefficients by the method of least squares as suggested by Barker [5].

Direct Evaluation of Equilibrium Vapor Composition: From thermodynamic reasoning, the general form of the Gibbs-Duhem equation

$$SdT - VdP + \sum n_i d\mu_i = 0 \quad (3-1)$$

implies a relation between simultaneous changes of temperature, pressure and the chemical potentials of the individual constituents of a single phase mixture. At constant temperature, equation (3-1) reduces to

$$\sum n_i d\mu_i = VdP \quad (3-2).$$

This equation may, of course, be applied to any phase, however, here it is applied specifically to the liquid phase. Therefore,  $V$  is the volume of the liquid solution.

For a system with liquid and vapor phases in equilibrium, the criterion of equilibrium is

$$\mu_i^{\text{liquid}} = \mu_i^{\text{vapor}} \quad (3-3).$$

Further, if the vapor phase is a perfect gas mixture, the chemical



potentials may be expressed as

$$\mu_1 = \mu_1^{\circ} + RT \ln p_1 \quad (3-4),$$

where  $\mu_1^{\circ}$  is a function only of temperature. At constant temperature,

$$d\mu_1 = RT \, d\ln p_1 \quad (3-5).$$

Substituting (3-5) in (3-2) gives

$$RT \sum n_i d\ln p_i = V dP \quad (3-6).$$

Equation (3-6) gives a relationship between changes in the total pressure  $P$  and the partial pressures  $p_i$ .

Dividing equation (3-6) through by the total number of moles,  $\sum n_i$ , in the condensed phase, we obtain

$$\sum x_i d\ln p_i = v_l dP / RT \quad (3-7).$$

Let  $RT = P v_g$ , then equation (3-7) may be rewritten as

$$\sum x_i d\ln p_i = (v_l / v_g) d\ln P \quad (3-8).$$

For a binary system with components 1 and 2, the partial pressures are  $p_1 = y_1 P$  and  $p_2 = (1 - y_1) P$ , respectively.

Substituting these relations in (3-8), gives

$$x_1 d\ln(y_1 P) + (1 - x_1) d\ln[(1 - y_1) P] = (v_l / v_g) d\ln P \quad (3-9).$$

And, on rearranging this equation we obtain

$$(d\ln P)_T = \frac{(y_1 - x_1)}{y_1(1 - y_1)[1 - (v_l / v_g)]} dy_1 \quad (3-10).$$

Equation (3-10) gives the relationship between the total vapor pressure measurements and the compositions of liquid and vapor phases of a binary system in equilibrium at constant temperature. At low pressure the term  $[1 - (v_l / v_g)]$  may be considered unity with little error. Then, the equation simplifies to

$$(d\ln P)_T = \frac{(y_1 - x_1)}{y_1(1 - y_1)} dy_1 \quad (3-11).$$

The application of equation (3-11) makes possible the rigorous thermodynamic calculation of vapor composition data from total vapor pressure-liquid composition data.

Evaluation of Constants of Equations Representing Activity Coefficients: For a binary liquid system in equilibrium with an ideal vapor phase, the relationship between liquid composition and total vapor pressure is

$$P = x_1 \gamma_1 P_1^0 + (1 - x_1) \gamma_2 P_2^0 \quad (3-12).$$

It is assumed that the activity coefficients  $\gamma_1$  and  $\gamma_2$  in equation (3-12) may be represented by a particular activity coefficient equation. The problem is therefore to determine the constants in the activity coefficient equation by a process of successive approximations so that the total vapor pressure values calculated from equation (3-12) agree with the experimentally observed values.

The procedure for carrying out these calculations has been detailed by Barker [5], and a complete computer program has been published by Prausnitz et. al. [1].

### 3.2 Calculation and Results

Step-wise Integration of Gibbs-Duhem Equation: In the calculation of equilibrium vapor composition data from total vapor pressure-liquid composition data for the n-hexane--acetonitrile system and the cyclohexane--acetonitrile system, the step-wise integration procedure was carried out by using equation (3-11) in the form of

$$\delta \ln P = \frac{(y_1 - x_1)}{y_1(1 - y_1)} \delta y_1 \quad (3-13).$$

The estimation of the vapor phase fugacity coefficients of both n-hexane--acetonitrile and cyclohexane--acetonitrile systems, according to the method suggested by Prausnitz et. al. [1] and using the second virial coefficient of acetonitrile reported by Prausnitz and Carter [6], justified the ideal vapor phase assumption made in the derivation of equation (3-13).

An increment of  $\delta x_1 = 0.005$  mole fraction was employed in the step-wise calculation. Values of P and x needed for the calculation were taken from smooth curves drawn through the experimental data points. The integration was started at  $x_1^{(0)} = 0$  where  $y_1^{(0)} = 0$  and  $P^{(0)} = p_2^0$ . For the first increment we have

$$\delta \ln P = \ln P^{(1)} - \ln P^{(0)}$$

$$\delta y_1 = y_1^{(1)}$$

and,

$$y_1^{(1)} = \frac{\delta \ln P + x_1^{(1)}}{1 + \delta \ln P} \quad (3-14).$$

The equilibrium vapor composition at the end of the first increment,  $y_1^{(1)}$ , was thus obtained. At the end of the second increment, the equilibrium vapor composition was obtained by trial and error calculation for  $y_1^{(2)}$  from equation (3-13) with  $x_1^{(2)} = 0.01$  and

$$\delta \ln P = \ln P^{(2)} - \ln P^{(1)}$$

$$\delta y_1 = y_1^{(2)} - y_1^{(1)}.$$

Subsequent integrations were carried out in the same manner until

$x_1$  reached the solubility limits.

Equilibrium vapor compositions on the other side of the miscibility gap were obtained by starting the integration from  $x_1 = 1.0$ . The results are listed in Tables 3-1 and 3-2, and plotted in Figures 3-1 and 3-2. The equilibrium vapor composition should remain constant over the two-liquid phase region hence this composition obtained from the calculations beginning at  $x_1 = 0$  should match that obtained from the calculations beginning at  $x_1 = 1.0$ . Reasonable matchings were obtained for both systems. The mismatch in the n-hexane--acetonitrile system was only 0.016 mole fraction, while in the cyclohexane--acetonitrile system it was 0.027 mole fraction.

The activity coefficients of the components in the liquid phase at 45° C. were calculated from the equilibrium data using following relationships:

$$\begin{aligned} \gamma_1 &= P_{y1}/p_1^\circ x_1 \\ \gamma_2 &= P_{y2}/p_2^\circ x_2 \end{aligned} \tag{3-15}.$$

The values obtained are also listed in Tables 3-1 and 3-2, and plotted in Figures 3-3 and 3-4.

Evaluation of Constants in Activity Coefficient Equations: The constants in the following activity coefficient equations were evaluated using the IBM 360 computer with a least squares program similar to that of Prausnitz et. al. [1].

Table 3-1. Calculated Equilibrium Vapor Compositions and Activity Coefficients by Step-wise Integration of Gibbs-Duhem Equation

System: n-Hexane(1)--Acetonitrile(2)  
at 45° C.

$x_1$	P	$y_1$	$y_1$	$y_2$
0.000	213.0	0.000		
0.005	247	0.134		
0.010	273	0.216	17.2	1.02
0.015	295	0.275		
0.020	315	0.322	14.8	1.02
0.025	332	0.358		
0.030	349	0.391	13.3	1.03
0.035	365	0.419		
0.040	380	0.444	12.3	1.03
0.045	394	0.465		
0.050	409	0.486	11.6	1.04
0.055	423	0.505		
0.060	463	0.521	11.0	1.04
0.065	448	0.535		
0.070	459	0.548	10.5	1.05
0.075	470	0.560		
0.080	479	0.570	9.94	1.06
0.085	488	0.579		
0.090	495	0.586	9.39	1.06
0.095	502	0.593		
0.100	508	0.599	8.86	1.06
0.105	513	0.604		
0.110	516	0.607	8.29	1.07
0.115	519	0.609		
0.121	520.5	0.610	7.64	1.08

$x_2$	$x_1$		$y_2$	$y_1$		
0.000	1.000	343.3	0.000	1.000		
0.005	0.995	365	0.062	0.938		
0.010	0.990	386	0.116	0.884	1.00	21.0
0.015	0.985	404	0.158	0.842		
0.020	0.980	421	0.195	0.805	1.01	19.3
0.025	0.975	435	0.224	0.776		
0.030	0.970	447	0.247	0.753	1.01	17.3
0.035	0.965	457	0.266	0.734		
0.040	0.960	466	0.282	0.718	1.02	15.4
0.045	0.955	474	0.296	0.704		
0.050	0.950	481	0.308	0.692	1.02	13.9
0.055	0.945	487	0.318	0.682		
0.060	0.940	492	0.326	0.674	1.03	12.6
0.070	0.930	500	0.340	0.660	1.03	11.4
0.080	0.920	507	0.351	0.649	1.04	10.5
0.090	0.910	512	0.359	0.641	1.05	9.56

Table 3-1. Cont'd.

$x_2$	$x_1$	P	$y_2$	$y_1$	$\gamma_1$	$\gamma_2$
0.100	0.900	514	0.362	0.638	1.06	8.74
0.110	0.890	517	0.367	0.633	1.07	8.10
0.120	0.880	519	0.371	0.629	1.08	7.53
0.130	0.870	520	0.373	0.627	1.08	7.01
0.1475	0.8525	520.5	0.374	0.626	1.11	6.20

Table 3-2. Calculated Equilibrium Vapor Compositions and Activity Coefficients by Step-wise Integration of Gibbs-Duhem Equation

System: Cyclohexane(1)--Acetonitrile(2)  
at 45° C.

$x_1$	P	$y_1$	$\gamma_1$	$\gamma_2$
0.000	213.0	0.000		
0.005	225	0.057		
0.010	237	0.108	11.0	1.00
0.015	249	0.154		
0.020	261	0.196	11.0	1.01
0.025	273	0.235		
0.030	284	0.268	10.9	1.01
0.035	295	0.298		
0.040	306	0.326	10.7	1.01
0.045	317	0.352		
0.050	328	0.376	10.6	1.01
0.055	338	0.397		
0.060	348	0.417	10.4	1.01
0.065	357	0.434		
0.070	365	0.448	10.0	1.02
0.075	373	0.462		
0.080	380	0.474	9.6	1.02
0.085	387	0.485		
0.090	393	0.494	9.2	1.03
0.100	402	0.508	8.7	1.03
0.110	407	0.516	8.2	1.04
0.120	409	0.519	7.6	1.05

Table 3-2. Cont'd.

x <sub>2</sub>	x <sub>1</sub>	P	y <sub>2</sub>	y <sub>1</sub>	Y <sub>1</sub>	Y <sub>2</sub>
0.000	1.000	233.7	0.000	1.000		
0.005	0.995	256	0.088	0.912		
0.010	0.990	278	0.162	0.838	1.01	21.2
0.015	0.985	296	0.215	0.785		
0.020	0.980	310	0.253	0.747	1.01	18.4
0.025	0.975	322	0.283	0.717		
0.030	0.970	334	0.311	0.689	1.02	16.3
0.035	0.965	344	0.333	0.657		
0.040	0.960	352	0.350	0.650	1.02	14.5
0.045	0.955	360	0.366	0.634		
0.050	0.950	367	0.380	0.620	1.03	13.1
0.055	0.945	374	0.393	0.607		
0.060	0.940	379	0.402	0.598	1.03	11.9
0.065	0.935	384	0.411	0.589		
0.070	0.930	388	0.418	0.582	1.04	10.9
0.075	0.925	393	0.427	0.573		
0.080	0.920	396	0.432	0.568	1.05	10.0
0.085	0.915	399	0.437	0.563		
0.090	0.910	402	0.442	0.558	1.05	9.27
0.100	0.900	406	0.449	0.551	1.06	8.86
0.113	0.887	409.0	0.454	0.546	1.08	7.72

(1) Three-parameter Margules Equation

$$\begin{aligned}\ln y_1 &= x_2^2 [A + 2x_1(B - A - D) + 3x_1^2 D] \\ \ln y_2 &= x_1^2 [B + 2x_2(A - B - D) + 3x_2^2 D]\end{aligned}\quad (3-16)$$

(2) Two-parameter Margules Equation

$$\begin{aligned}\ln y_1 &= x_2^2 [A + 2x_1(B - A)] \\ \ln y_2 &= x_1^2 [B + 2x_2(A - B)]\end{aligned}\quad (3-17)$$

(3) van Laar Equation

$$\begin{aligned}\ln y_1 &= A/[1 + (A/B)x_1/x_2]^2 \\ \ln y_2 &= B/[1 + (B/A)x_2/x_1]^2\end{aligned}\quad (3-18)$$

(4) NRTL (nonrandom, two-liquid) Equation

$$\begin{aligned}\ln y_1 &= x_2^2 \left\{ T_{21} \frac{\exp(-2A_{12}T_{21})}{[x_1 + x_2 \exp(-A_{12}T_{21})]^2} \right. \\ &\quad \left. + T_{12} \frac{\exp(-A_{12}T_{12})}{[x_2 + x_1 \exp(-A_{12}T_{12})]^2} \right\} \\ \ln y_2 &= x_1^2 \left\{ T_{12} \frac{\exp(-2A_{12}T_{12})}{[x_2 + x_1 \exp(-A_{12}T_{12})]^2} \right. \\ &\quad \left. + T_{21} \frac{\exp(-A_{12}T_{21})}{[x_1 + x_2 \exp(-A_{12}T_{21})]^2} \right\}\end{aligned}\quad (3-19)$$

The constants determined are listed in Table 3-3.

The equilibrium total vapor pressures, equilibrium vapor compositions and liquid phase activity coefficients obtained from the fit of the two-parameter and three-parameter Margules equations are listed in Tables 3-4 and 3-5, and plotted in Figures 3-5(a),(b), 3-6(a),(b), 3-1, 3-2, 3-3 and 3-4, respectively, for



comparison with the experimental data and those calculated from the step-wise integration of the Gibbs-Duhem equation. The results obtained from the fit of the van Laar equation were essentially the same as those obtained from the fit of the two-parameter Margules equation, and those obtained from the fit of the NRTL equation were similar to those obtained from the fit of the three-parameter Margules equation if the constant  $A_{12}$  was not fixed; but were similar to those obtained from the fit of the two-parameter Margules equation if the constant  $A_{12}$  was fixed at 0.200.

Table 3-3. Constants of activity coefficient equations evaluated.

	n-Hexane-- Acetonitrile	Cyclohexane-- Acetonitriles
2-Parameter Margules Equation	A = 1.1853 B = 1.2152	A = 1.1299 B = 1.2271
3-Parameter Margules Equation	A = 1.2655 B = 1.3217 D = .68263	A = 1.1587 B = 1.2570 D = .22239
van Laar Equation	A = 1.1851 B = 1.2158	A = 1.1307 B = 1.2286
NRTL Equation	$A_{12}$ = .37201 $T_{12}$ = 2.1336 $T_{21}$ = 1.9528	$A_{12}$ = .26588 $T_{12}$ = 1.8976 $T_{21}$ = 1.5245
NRTL Equation	$A_{12}$ = 0.2000 $T_{12}$ = 1.7170 $T_{21}$ = 1.5459	$A_{12}$ = 0.2000 $T_{12}$ = 1.8305 $T_{21}$ = 1.3672

Table 3-4. Calculated Equilibrium Total Vapor Pressures,  
Vapor Compositions and Activity Coefficients  
by Margules Equation Fit

System: n-Hexane(1)--Acetonitrile(2) at 45° C.

x <sub>1</sub>	P <sub>exp.</sub>	Two-parameter Margules Equation				Three-parameter Margules Equation			
		P <sub>calc.</sub>	% Dev. of P	y <sub>1</sub>	y <sub>2</sub>	P <sub>calc.</sub>	% Dev. of P	y <sub>1</sub>	y <sub>2</sub>
0.0135	291.2	276.37	5.09	.239	14.27	286.45	1.63	.266	16.43
0.0159	300.3	286.68	4.54	.268	14.09	297.77	-0.84	.295	16.11
0.0203	314.2	304.88	2.97	.315	13.77	317.30	-0.99	.341	15.54
0.0324	357.0	350.53	1.81	.410	12.93	363.78	-1.90	.431	14.10
0.0397	381.4	375.18	1.63	.453	12.46	387.36	-1.56	.469	13.32
0.0445	403.2	390.28	3.20	.476	12.16	401.27	0.48	.489	12.84
0.0502	407.2	407.15	0.01	.500	11.81	416.31	-2.24	.509	12.30
0.0550	420.1	420.50	-0.10	.517	11.52	427.83	-1.84	.524	11.87
0.0638	443.2	443.06	0.03	.545	11.03	446.54	-0.75	.546	11.13
0.0686	459.0	454.39	1.00	.558	10.76	455.55	0.75	.556	10.76
0.0710	462.0	459.80	0.48	.564	10.64	459.77	0.48	.561	10.58
0.0819	482.1	482.45	-0.07	.587	10.08	476.76	1.11	.579	9.818
0.0910	493.0	499.08	-1.23	.603	9.639	488.55	0.90	.591	9.240
0.0945	500.8	504.96	-0.83	.609	9.476	492.57	1.64	.595	9.031
0.121	520.5	541.44	-4.02	.640	8.347	515.67	0.93	.616	7.656
0.8525	520.5	547.97	-5.28	.568	1.064	533.18	-2.44	.597	1.088
0.8780	518.7	536.31	-3.40	.586	1.043	528.11	-1.81	.606	1.062
0.9154	509.1	506.93	0.43	.633	1.021	510.55	-0.28	.634	1.307
0.9305	497.0	489.48	1.51	.662	1.014	497.79	-0.16	.655	1.021
0.9416	491.6	464.07	3.57	.689	1.010	485.34	1.27	.676	1.015
0.9539	473.3	454.05	4.07	.726	1.006	467.65	1.19	.707	1.010
0.9706	446.0	421.13	5.58	.793	1.003	435.18	2.43	.769	1.004

Parameters: A=1.1853 B=1.2152  
Parameters: A=1.2655 B=1.3217  
D=.68263



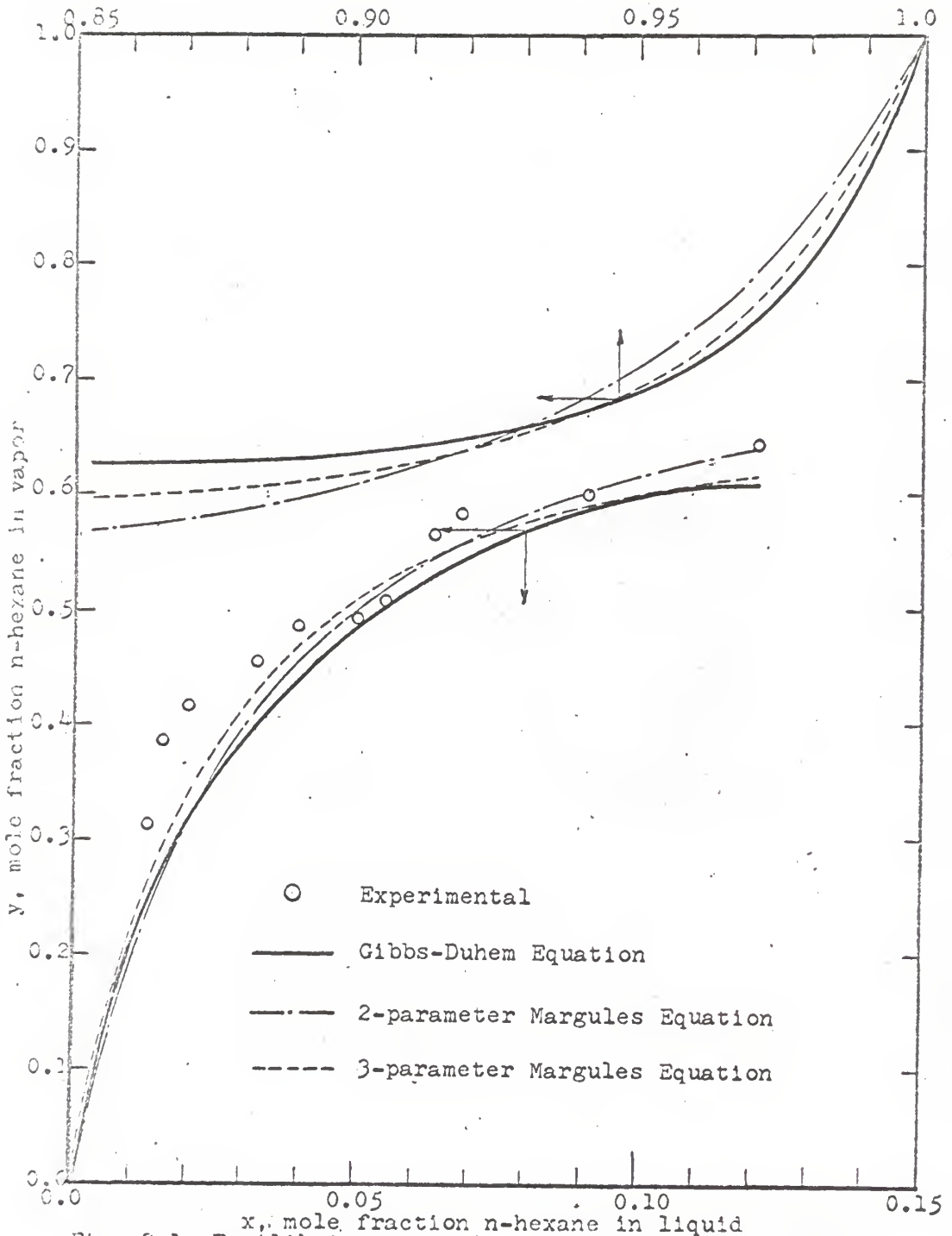


Fig. 3-1. Equilibrium composition values for the system n-Hexane-Acetonitrile at 45° C.

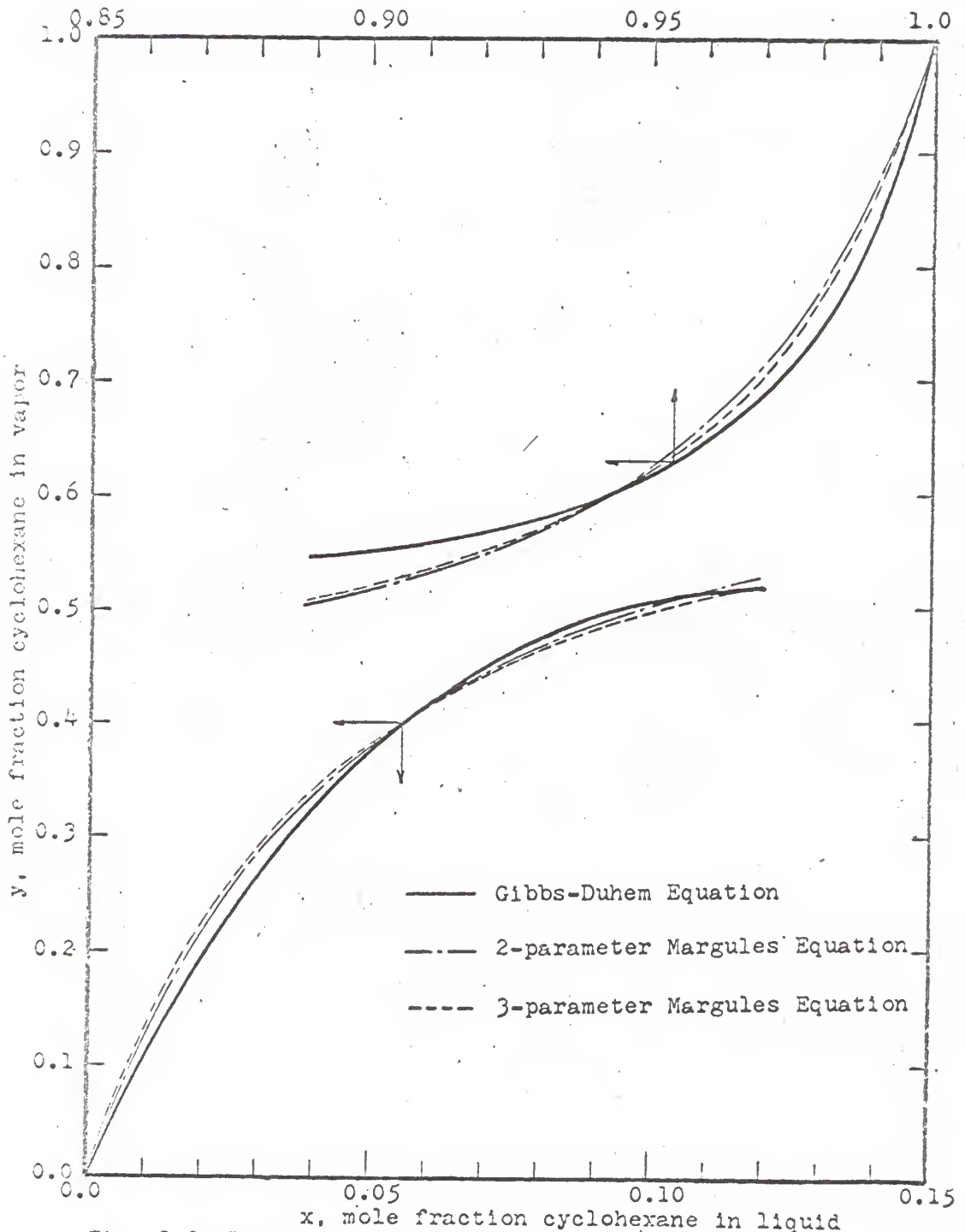


Fig. 3-2. Equilibrium composition values for the system Cyclohexane-Acetonitrile at 45° C.

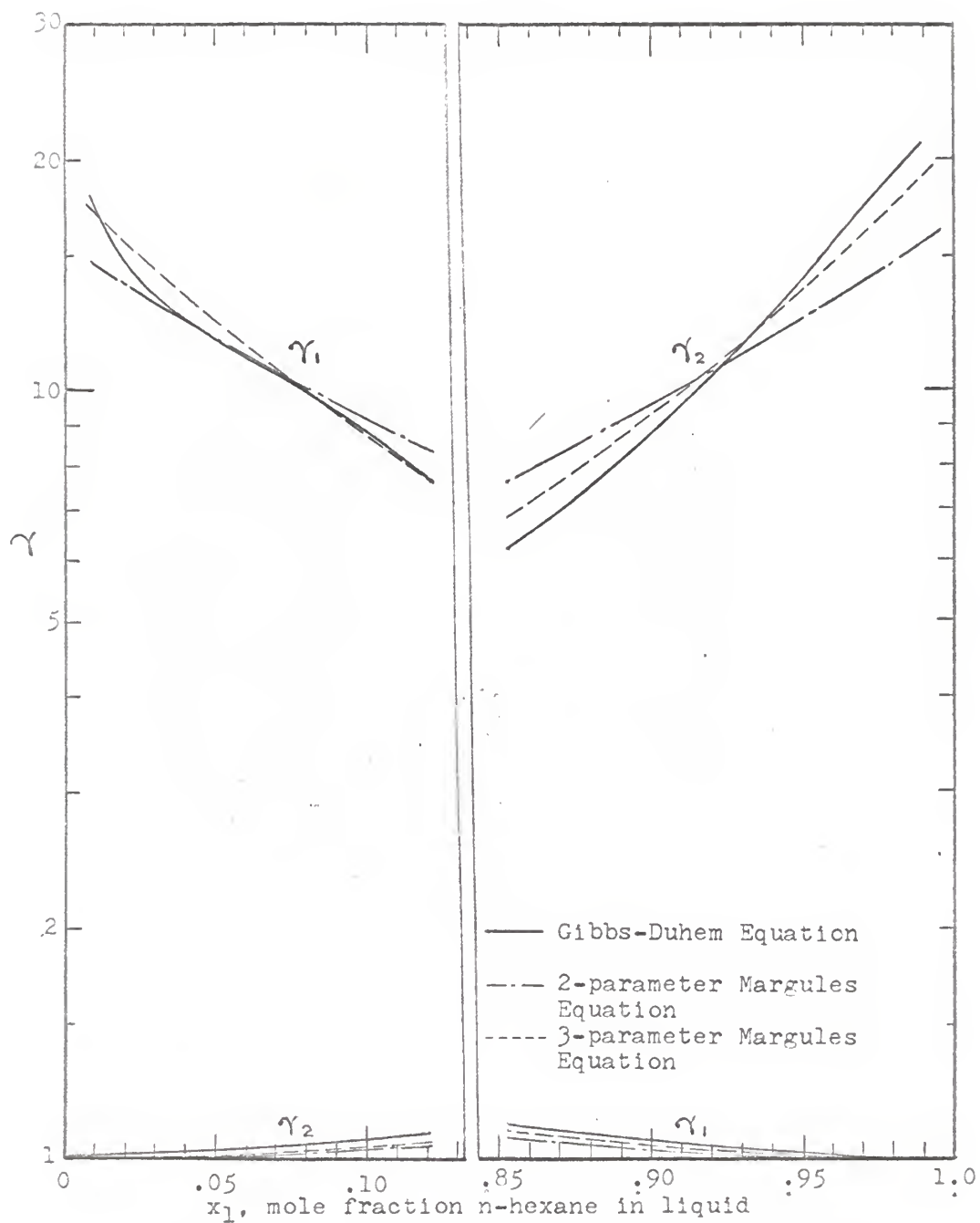


Fig. 3-3. Activity Coefficients, System n-Hexane(1)--Acetonitrile(2) at 45° C.

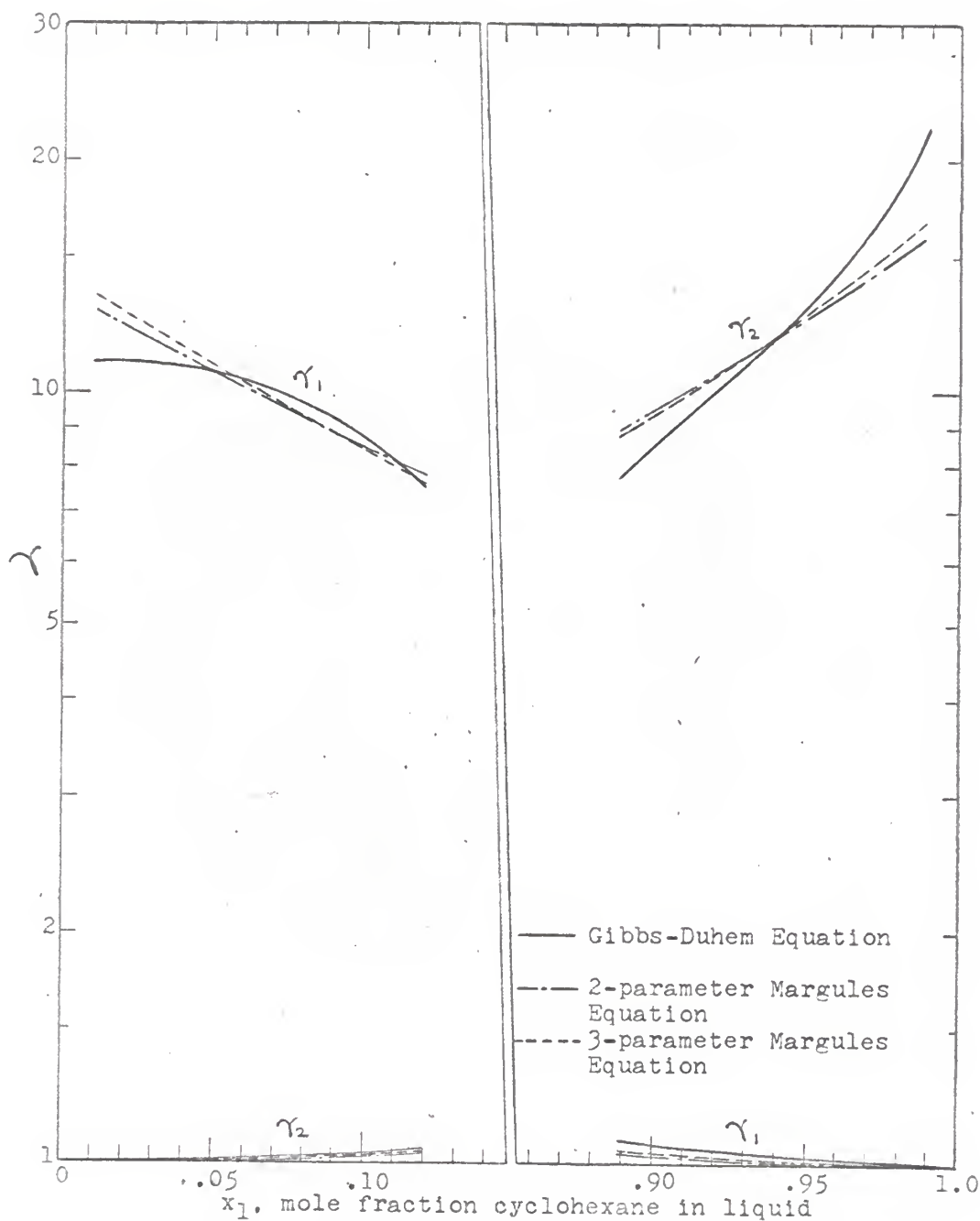


Fig. 3-4. Activity Coefficients, System Cyclohexane(1)-Acetonitrile(2) at 45° C.

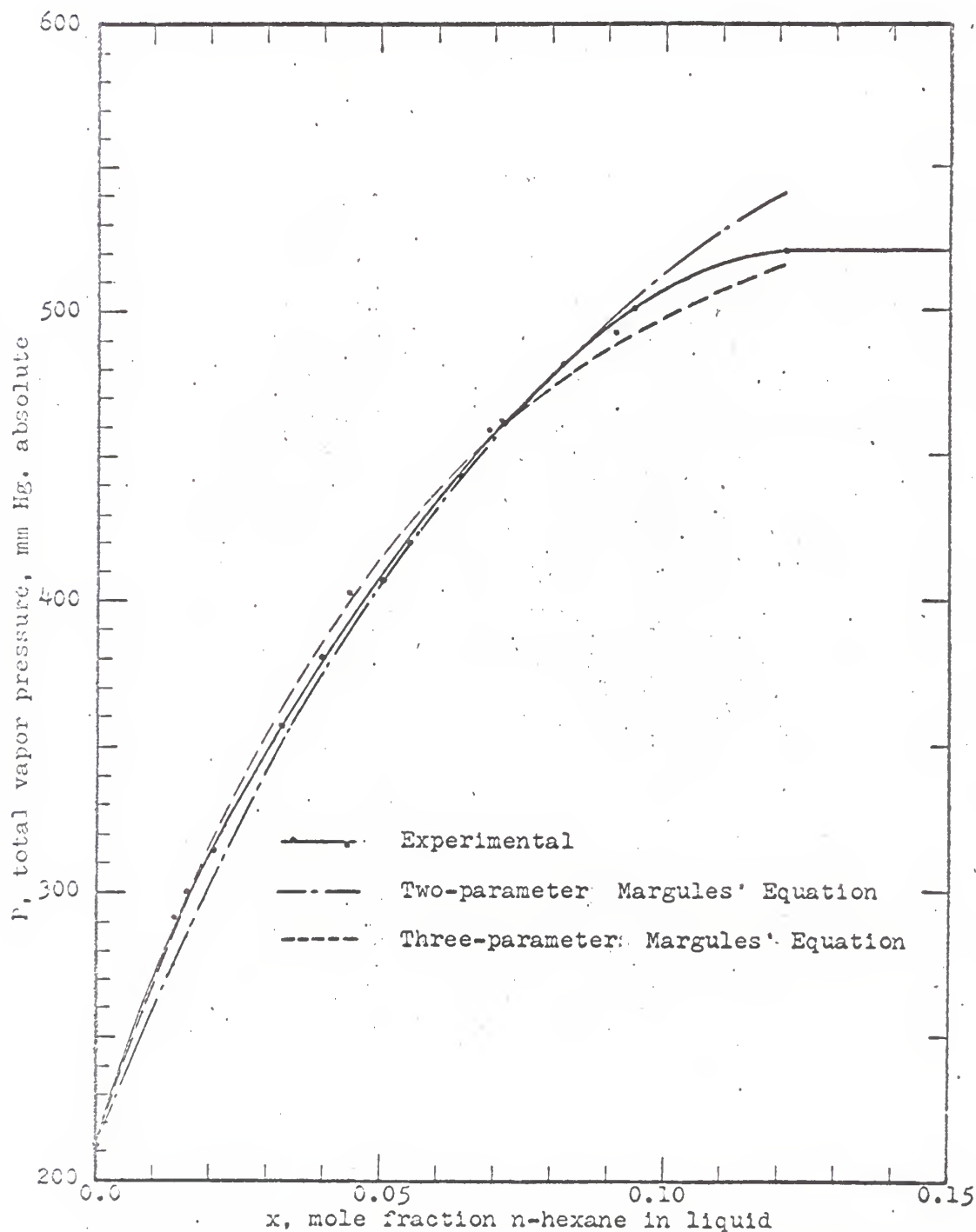


Fig. 3-5a. Total vapor pressure vs. liquid composition, system n-Hexane-Acetonitrile at 45° C.



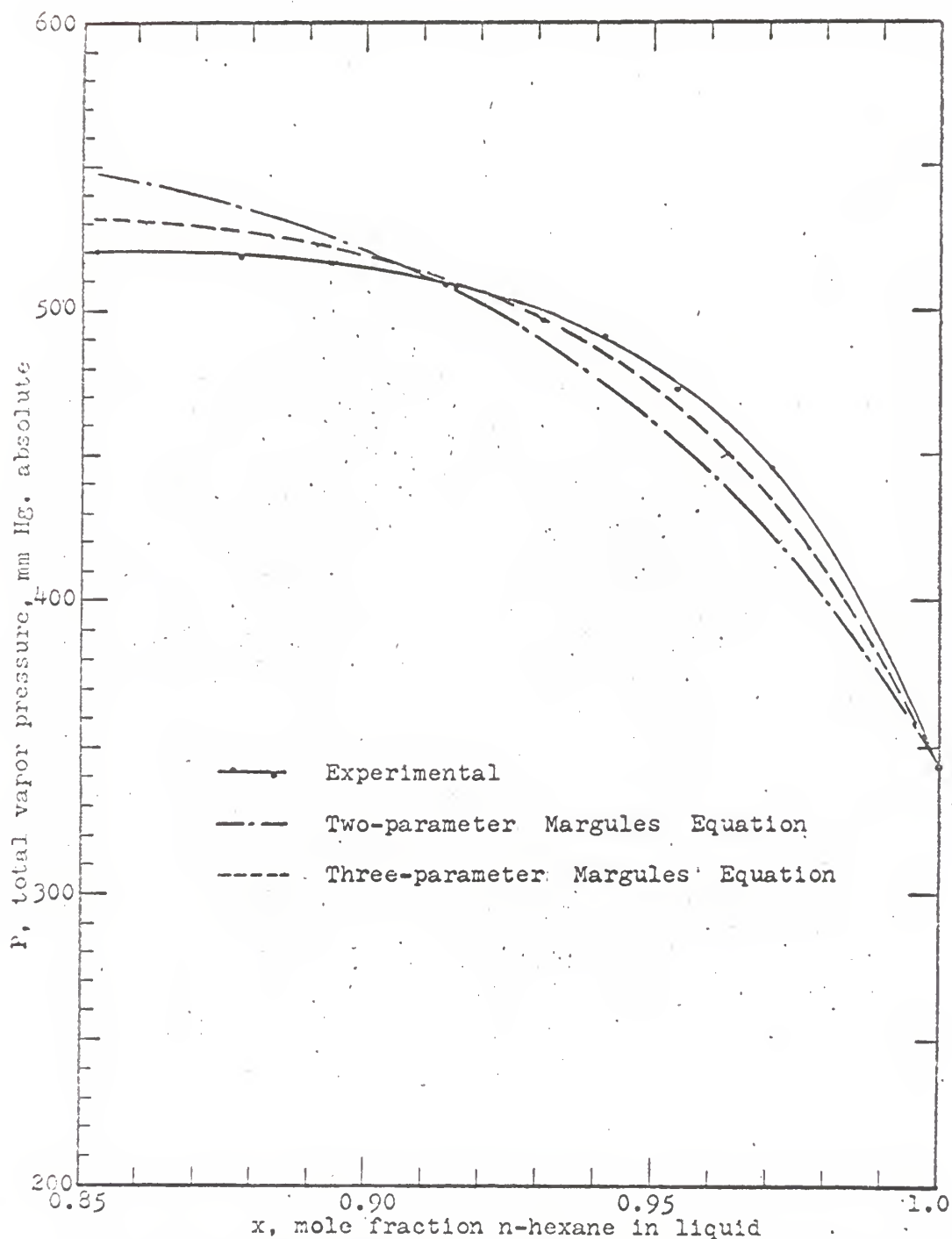


Fig. 3-5b. Total vapor pressure vs. liquid composition, system n-Hexane-Acetonitrile at 45° C.

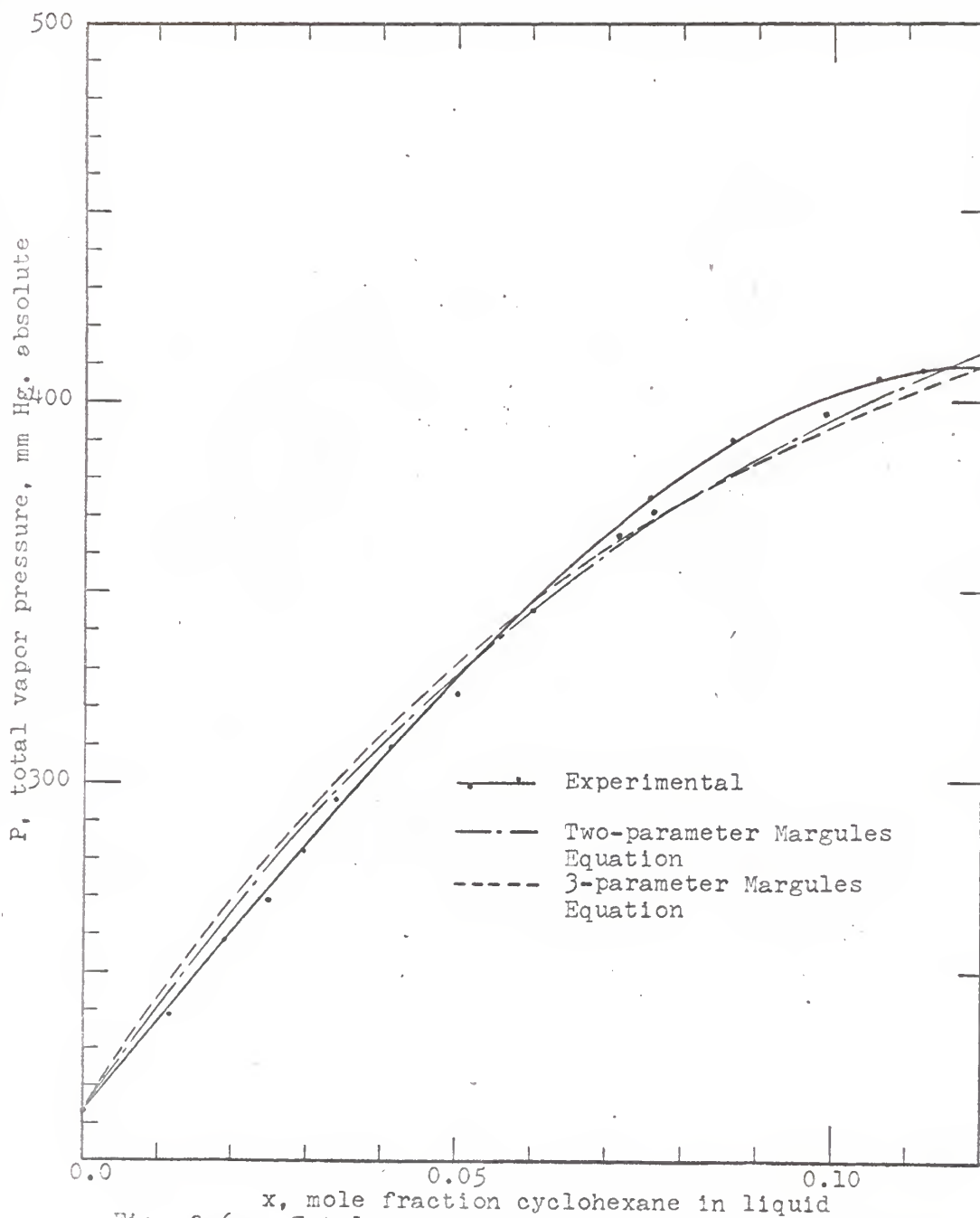


Fig. 3-6a. Total vapor pressure vs. liquid composition, system Cyclohexane-Acetonitrile at 45° C.

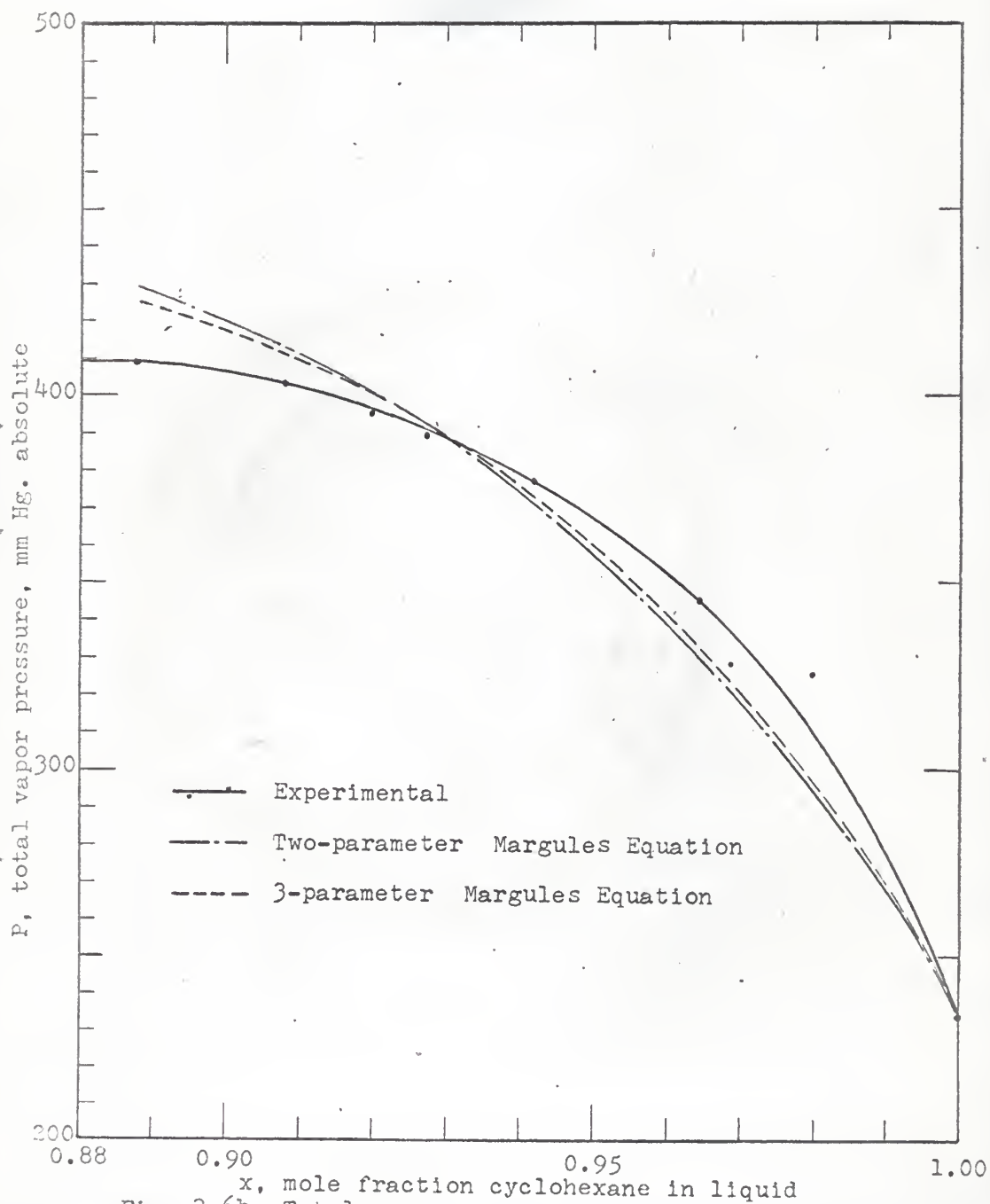


Fig. 3-6b. Total vapor pressure vs. liquid composition, system Cyclohexane-Acetonitrile at 45° C.

#### IV. DISCUSSION AND CONCLUSIONS

The experimental total vapor pressure-liquid composition data obtained in this work seemed to be of good quality because smooth curves were obtained on their plots and good matchings in the vapor compositions over the two-liquid phases were obtained with the direct Gibbs-Duhem equation calculations. The fact that the activity coefficient equations do not fit the total pressure-liquid composition data as well as expected could mean only that these equations are simply not capable of representing activity coefficients sufficiently well in systems with large positive deviations such as these.

The experimentally determined vapor compositions of the n-hexane--acetonitrile system were only in fair agreement with those calculated from the total pressure-liquid composition measurements by the step-wise integration of the Gibbs-Duhem equation. This is believed to be due to errors in analysing the vapor samples. The fact that the area ratios of the chromatographic peaks were sensitive to the sample size and the correction factors which converted the area ratios to the weight ratios of the components were sensitive to the composition of the mixture, for both n-hexane--acetonitrile and cyclohexane--acetonitrile systems, indicated the possibility of partial adsorption of the components in the gas chromatograph. The technique used in introducing vapor samples into the gas chromatograph could not adequately reproduce the corresponding sample sizes used in the construction of the calibration curves. Because the extent of the

adsorption effect could be dependent on sample size, the inability to reproduce the sample size could cause errors in the analyses.

Improvement of the technique for vapor sample introduction might possibly improve the accuracy of the vapor composition determination; however, the selection of a chromatographic column which will not adsorb the components of the sample introduced would not only improve the accuracy of the vapor composition determinations, but also improve the precision of the chromatographic measurements.

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## NOMENCLATURE

A	Constant in activity coefficient equation
B	Constant in activity coefficient equation
D	Constant in activity coefficient equation
n	Number of moles of component; Number of data points
P	Total vapor pressure of system
p	Partial vapor pressure of component
R	Gas constant
S	Entropy of system
T	Absolute temperature; Constant in NRTL equation
V	Total volume
$v_g$	Volume per mole of vapor phase
$v_l$	Volume per mole of condensed phase
x	Mole fraction in condensed phase
y	Mole fraction in vapor phase
$\gamma$	Liquid phase activity coefficient
$\delta$	Sign indicating excess of final over initial value
$\mu$	Chemical potential
$\sigma_{rel.}$	Standard relative deviation
$\Sigma$	Summation operator sign

## Subscripts

1	Component 1
2	Component 2
i	$i^{th}$ component

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THERMODYNAMICS OF  
ACETONITRILE-HYDROCARBON SYSTEMS

by

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AN ABSTRACT OF A MASTER'S THESIS

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1968

Apparatus and experimental techniques were developed for studying phase equilibrium of partially miscible systems. Vapor-liquid equilibrium data (including the two-liquid phase region) were obtained for the binary systems n-hexane--acetonitrile and cyclohexane--acetonitrile at 45° C.

The equilibrium total vapor pressure measurements were conducted by the static method using a newly designed equilibrium cell, and the corresponding equilibrium vapor and liquid compositions were determined by gas chromatographic analysis. The equilibrium vapor compositions and the liquid phase activity coefficients were also calculated from the total vapor pressure-liquid composition measurements by (1) the step-wise integration of the Gibbs-Duhem equation and (2) the non-linear least squares fit of the activity coefficient equations including the three-parameter and two-parameter Margules equations, the van Laar equation and the NRTL (nonrandom, two-liquid) equation using the IBM 360 computer. The results obtained were compared graphically on plots of (1) vapor composition versus liquid composition, (2) liquid phase activity coefficient versus liquid composition and (3) total vapor pressure versus liquid composition.