x_{HC}, Φ_{HC} = total mole fraction or volume fraction of hydrocarbon in the predominantly solvent phase, a
x_{ij} =mole fraction of component i in phase j
x_s, Φ_s =mole fraction or volume fraction of the solvent in the predominantly solvent phase, a

Greek Letters

β_j^i =separation factor for components i and j with solvent
γ_{ij} =activity coefficient of component i in phase j
$\Delta H_{v,i}$ =molar heat of vaporization of component i
δ_i, δ_s =solubility parameter of component i or solvent $=[(\Delta H_v - RT)/V]^{1/2}$
ϵ_j^i =selectivity parameter for the separation of components i and j with a solvent
ρ $=(V_j/V_i) - 1$

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Isothermal Activity Coefficients for the System Cyclohexane—*n*-Heptane—Toluene at 25°C.

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Isothermal vapor-liquid equilibrium data at 25°C. are presented for the ternary and binary systems containing cyclohexane, *n*-heptane, and toluene. These data were obtained by static equilibration in the presence of diluent nitrogen by chromatographic analysis of the saturated vapor. The data obtained were of at least comparable accuracy to those available at the normal boiling point, and the procedure appears to offer several substantial advantages. Neither a priori prediction of activity coefficients from regular solution theory nor extrapolation of data taken at the normal boiling point is a satisfactory substitute for the isothermal data.

Isothermal vapor-liquid equilibrium data are presented for the system cyclohexane–*n*-heptane–toluene at 25°C. These data were obtained by analysis of vapors in equilibrium with a liquid of known composition, and were correlated by the Redlich-Kister equations. The liquid and vapor were equilibrated by a static method and the vapor was analyzed by gas chromatography. Success in the chromatographic analysis permitted use of the simple and reliable static equilibration method as opposed to the more common dynamic methods.

Dynamic, or circulating, stills have been used widely, primarily because they provide large amounts of condensed vapor for analysis. However, these stills are difficult to construct, require highly skilled operators, and are subject to several systematic errors resulting from: (1) imperfect mixing of the boiling liquid; (2) entrainment (this is particularly serious at low gas density where entrainment has a greater effect and where bumping is likely); and (3) undue enrichment of the condensing vapor. In addition it is more difficult to obtain isothermal data than isobaric in this type of equipment.

The vapor chromatograph operated successfully with relatively small uncondensed gas samples (25 ml.) and thus permitted use of the static technique even at the low vapor pressures encountered in this work. In addition, use of nitrogen as an insoluble diluent permitted operation at

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slightly above atmospheric pressure and provided a useful check of the data by material balance.

Average deviation of individual chromatographic analyses was within 1%. This is comparable to available isobaric data at the normal boiling point, and it should be noted in this regard that it becomes more difficult to maintain precision as vapor pressure is reduced. Use of the Redlich-Kister correlation technique with ratios of individual activities reduced errors in the final correlation. This is because the primary source of error was an inadequate control of column operating conditions and measurement of the reference area for nitrogen. As a result relative errors were smaller than absolute errors in any one column run.

EXPERIMENTAL

Reagents

All three reagents were Fisher Certified Grade, used without further purification. Refractive indexes were measured in our laboratory, and are listed in Table 1. The nitrogen used in the experiments had a purity of at least 99.8%.

Apparatus

The equipment, indicated diagrammatically in Figures 1 and 2, comprised three parts: equilibrium still, gas chromatograph, and recorder.

The still had a volume of about 700 ml.; both it and the bulk of the mercury reservoir were immersed in a water bath maintained at 25° ± 0.01°C. All flexible tubing, shown in the diagrams, was made of Teflon which was impermeable to the vapors used. The total volume of tubing between the vapor space in the still and the sampling valve of the chromatograph was about 15 ml. Mercury flow was controlled by movement of a tapered needle relative to the constriction at the end of the delivery tube. Room temperature was maintained at least 1°C. higher than the water bath to prevent condensation in the sample line and vapor sampling valve.

The chromatograph was a Perkin-Elmer 150-C equipped with a 10-ft. coil, ¼-in. I.D. It was packed with 30 weight percent Dow-Corning silicone on Chromosorb P. Helium was used as carrier gas at a flow rate of 50 ml./min. The room temperature was also controlled at 27° ± 1°C. so as to have better temperature control in the column.

The recorder was a Sargent Recorder Model SR equipped with an integrator. Recording was made of voltage output from the chromatograph as a function of time, using a 12.5 mv. range.

Procedure

After thorough cleaning and drying, the still was placed in an ice bath, and the air in the still was replaced by nitrogen. Then approximately 150 ml. of cold solvent mixture of known composition were poured into the still and the still was closed and set in the water bath. The reservoir was filled with mercury and the still was allowed to come to thermal equilibrium with the bath. Gas was released through the stopcock as needed to control total pressure of the vapor

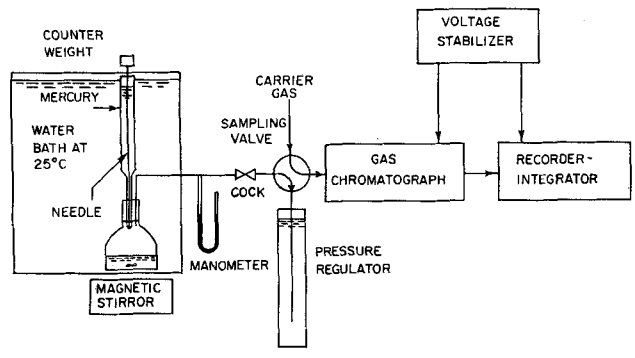

Fig. 1. Schematical diagram of apparatus.

TABLE 1. REFRACTIVE INDEXES AT 25°C. FOR SODIUM D LIGHT

Substance	Measured	Literature value (3)
Cyclohexane	1.4235	1.42354
n-Heptane	1.3852	1.38512
Toluene	1.4941	1.49414

phase. This pressure was chosen to keep the partial pressure of nitrogen at about 735 mm. Hg for all runs (about atmospheric pressure in the laboratory). To shorten equilibrium time the liquid in the still was agitated mildly by a magnetic bar. A total holding time of about 1 hr. was sufficient for both thermal and diffusional equilibrium, and a minimum of 3 hr. was used for the actual experimental runs.

Equilibrium vapor was sent to the vapor sampler of the chromatograph by feeding mercury through the nozzle of the mercury delivery tube; a bamboo needle was used to control mercury flow. Just before sampling the pressure in the sample valve and the line from the still to the chromatograph was adjusted to equal that in the still. This was done by adjusting the water level of the pressure regulator as shown in Figure 1. This line and sample valve had previously been filled with helium, which was used as the carrier gas in all experiments.

Three samples of gas were analyzed from each such preparation of the still, and the areas under the recorded voltage-time curve were averaged for each species, including nitrogen. About 80 ml. of gas were displaced from the still for each of these three analyses. To minimize errors resulting from incomplete replacement of helium in the line and sample valve, 100 ml. of gas from the still were passed through the sample valve and connecting lines prior to these triplicate analyses.

Concentration of vapor in the exit stream from the chromatograph column was determined by measuring the thermal conductivity in the detector chambers. Partial pressures of each component in the vapor phase were calculated from the equation

$$p_i = \frac{f_i A_i}{\sum_{i=1}^{4} f_i A_i} \qquad (1)$$

These weighting factors f_i were determined from experiments using saturated solutions of the individual vapors in nitrogen. Nitrogen was always the major constituent, and it was found that the f_i could be considered constant at the values: 0.297_2, 0.227_0, and 0.243_3 for cyclohexane, *n*-heptane, and toluene, respectively.* Nitrogen arbitrarily was given a

* A series of experiments designed to check for effect of vapor concentration and interaction between the vapors was inconclusive. Small effects may exist, but they are of the same order of magnitude as the experimental error.

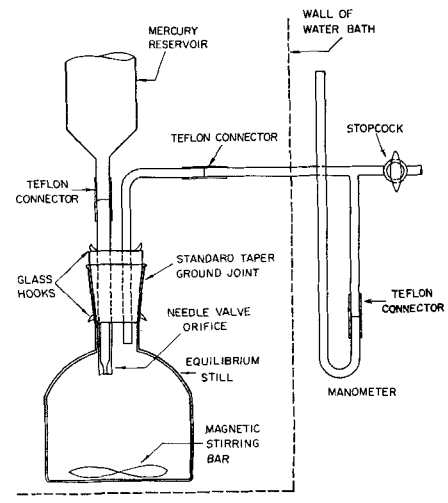

Fig. 2. Equilibrium still.

value of unity at 735 mm. Hg partial pressure. Corrections to f_{N_2} for change in partial pressure were made according to the equation

$$f_{N_2} = 1.0000 + 0.00027\,(p_{N_2} - 735)$$

This refinement was necessary for nitrogen because the peak voltage from the conductivity cell was very high and response of the cell to nitrogen concentration was appreciably nonlinear. Since estimated solubility of nitrogen into solvent is always below 0.0015 mole fraction in this experiment, the effect of the presence of nitrogen in the liquid phase on liquid phase activity coefficients of the other components was assumed negligible, and the concentration of nitrogen in liquid phase was neglected in all calculations.

Liquid phase activity coefficients were calculated from the expression

$$\gamma_i = \frac{p_i}{x_i P_i^{\circ}} \tag{2}$$

The assumption of ideal gas behavior was a good one in this case because the partial pressures of the vapors were low, and any small errors resulting from its use were nearly cancelled in further analysis of the data. This is because ratios of activity coefficients were used and because departures from the ideal gas law are similar for all three vapors. The vapor pressures used were cyclohexane, 97.582 mm. Hg; *n*-heptane, 45.718 mm. Hg; and toluene, 28.447 mm. Hg. These were calculated from Antoine's equation for 25°C., using constants given by the American Petroleum Institute (*1*).

Liquid compositions, known before evaporation in the still, were corrected for the small amount of evaporation taking place. This correction was always within 0.0005 mole fraction. The ability to choose liquid compositions precisely is a major advantage for this method and is especially useful in correlating ternary data.

CORRELATION OF THE DATA AND TEST OF THERMODYNAMIC CONSISTENCY

Ternary modifications of the Redlich-Kister equations for excess free energy and the Van Ness form of the Gibbs-Duhem equation were used in this work. The latter is of particular interest because its use is greatly facilitated by the static equilibration technique employed here. This is because data can be taken at precisely predetermined compositions.

Consistency

Discussion is begun with the Van Ness form of the Gibbs-Duhem equation (*14*):

$$\frac{\Delta V}{2.303\,RT}\,dp - \frac{\Delta H}{2.303\,RT^2}\,dT =$$

$$\Sigma(x_i\,d\log\gamma_i) = d\Sigma(x_i\log\gamma_i) - \Sigma\log\gamma_i\,dx_i \tag{3}$$

where for a liquid system

$$\Delta V = V - V_{\text{ideal}} \tag{4}$$

$$\Delta H = H - H_{\text{ideal}} \tag{5}$$

The activity coefficients of Equation (2) can be used in this expression if, as is true here, the ideal gas law is applicable. Temperature changes were identically zero in these experiments and both volume changes and pressure changes were very small. The left side of Equation (3) can then be neglected, and the remaining terms can now be integrated for a path on which mole fraction of a component is held constant to give

$$\int_a^b \log\gamma_1/\gamma_2\,dx_1 =$$

$$(x_1\log\gamma_1)_b + (x_3\log\gamma_3)_b - (x_2\log\gamma_2)_a - (x_3\log\gamma_3)_a \tag{6}$$

where x_3 has been held constant. The points a and b are located on the sides $x_1 = 0$, and $x_2 = 0$, respectively, of the triangular composition diagram.

Equation (6) shows that one can check the thermodynamic consistency of experimental values of $\log\gamma_1/\gamma_2$ on any line ab in the ternary diagram when binary activity coefficients at the end points of line ab are known.

For the special case where $x_3 = 0$, each right-hand term in Equation (6) becomes zero. This equation then reduces to the useful relation of Redlich-Kister equation for a binary system (*11*).

$$\int_{x_1=0}^{x_1=1} \log(\gamma_1/\gamma_2)\,dx_1 = 0 \tag{7}$$

This is an integrated form of the Gibbs-Duhem equation for a binary system at the conditions of constant temperature and pressure.

Use of ratios of activity coefficients in this equation is especially advantageous in reducing the effect of experimental error, as discussed in the introduction.

Correlation

For binary systems Redlich and Kister (*11*) proposed for dimensionless excess free energy, Q_{12}

$$Q_{12} = x_1\log\gamma_1 + x_2\log\gamma_2 \tag{8}$$

the expression

$$Q_{12} = x_1x_2\,[b_{12} + c_{12}(x_1 - x_2) + d_{12}(x_1 - x_2)^2 + \ldots] \tag{9}$$

From these equations and by use of the Gibbs-Duhem equation at constant temperature and pressure, the following equations can be derived:

$$\log\gamma_1/\gamma_2 = -b_{12}(x_1 - x_2) + c_{12}\,(6x_1x_2 - 1) + d_{12}(x_1 - x_2)\,(8x_1x_2 - 1) + \ldots \tag{10}$$

$$\log\gamma_1 = x_2^2\,[b_{12} + c_{12}(3x_1 - x_2) + d_{12}(x_1 - x_2) + \ldots] \tag{11}$$

$$\log\gamma_2 = x_1^2\,[b_{12} + c_{12}(x_1 - 3x_2) + d_{12}(x_1 - x_2)\,(x_1 - 5x_2) + \ldots] \tag{12}$$

The corresponding excess free energy function for a ternary system is

$$Q_{123} = (x_1\log\gamma_1 + x_2\log\gamma_2 + x_3\log\gamma_3) \tag{13}$$

For it Redlich and Kister proposed the expression

$$Q_{123} = Q_{12} + Q_{23} + Q_{31} + x_1x_2x_3\,[B + C_1(x_2 - x_3) + C_2(x_3 - x_1) + C_3(x_1 - x_2) + \ldots] \tag{14}$$

where the first three terms of right-hand side are the binary Q_{ij} and the term in brackets represents the ternary interactions. The ternary systems analogous to Equations (10) to (12) are:

$$\log(\gamma_1/\gamma_2) =$$

$$-[b_{12}(x_1 - x_2) + c_{12}\{(x_1 - x_2)^2 - 2x_1x_2\} + d_{12}\{(x_1 - x_2)^2 - 4x_1x_2\}(x_1 - x_2) + \ldots]$$

$$-x_3[b_{23} + c_{23}(2x_2 - x_3) + d_{23}(3x_2 - x_3)(x_2 - x_3) + \ldots] +$$

$$x_3\,[b_{31} + c_{31}(x_3 - 2x_1) + d_{31}(x_3 - 3x_1)(x_3 - x_1) + \ldots]$$

$$-x_3\,[B(x_1 - x_2) + C_1\{(x_1 - x_2)(x_2 - x_3) + x_1x_2\} + C_2\{(x_1 - x_2)(x_3 - x_1) + x_1x_2\} + C_3\{(x_1 - x_2)(x_1 - x_2) - 2x_1x_2\} + \ldots] \tag{15}$$

$$\log\gamma_1 =$$

$$x_2\,[b_{12}(1 - x_1) + c_{12}\{(1 - x_1)(2x_1 - x_2) + x_1x_2\} +$$

TABLE 2. EXPERIMENTAL DATA OF BINARY SYSTEMS AT 25°C.

Composition, mole fraction								Partial pressure, mm. Hg			
Cyclohexane(1)-*n*-heptane(2)				*n*-Heptane(2)-toluene(3)				Cyclohexane(1)-toluene(3)			
x_1	p_1	p_2	$\log_{10}(\gamma_1/\gamma_2)$	x_2	p_2	p_3	$\log_{10}(\gamma_2/\gamma_3)$	x_1	p_1	p_3	$\log_{10}(\gamma_7/\gamma_3)$
0.0468	4.989	42.99	0.0447	0.0500	3.589	26.10	0.2109	0.0505	7.413	26.95	0.1784
0.1010	10.69	40.86	0.0380	0.0999	6.750	25.05	0.1791	0.1013	14.04	24.85	0.1650
0.1877	19.83	37.34	0.0322	0.1991	12.33	23.25	0.1232	0.1989	26.05	22.98	0.1241
0.3005	31.06	32.44	0.0188	0.3003	17.15	21.52	0.0628	0.2836	35.44	22.80	0.0588
0.3821	38.92	28.60	0.0133	0.3979	21.19	18.76	0.0268	0.4002	46.58	18.67	0.0374
0.5001	50.62	23.83	−0.0023	0.4999	24.73	15.50	−0.0028	0.5000	54.71	16.02	−0.0019
0.5819	57.83	19.60	−0.0030	0.6002	28.84	13.23	−0.0440	0.6004	63.83	13.78	−0.0462
0.6999	68.71	14.55	−0.0228	0.6989	34.91	11.18	−0.0773	0.7000	71.16	10.96	−0.0907
0.7879	76.83	10.27	−0.0252	0.7985	36.47	7.362	−0.1092	0.7998	78.61	7.561	−0.1198
0.8998	87.26	5.188	−0.0567	0.8984	41.28	4.031	−0.1414	0.8996	87.34	4.301	−0.1801
0.9459	92.23	2.798	−0.0542	0.9494	43.12	2.183	−0.1834	0.9501	92.58	2.252	−0.2007

$$d_{12}\{(1-x_1)(3x_1-x_2)+2x_1x_2\}(x_1-x_2)+\ldots]$$
$$-x_2x_3[b_{23}+2c_{23}(x_2-x_3)+3d_{23}(x_2-x_3)^2+\ldots]+$$
$$x_3[b_{31}(1-x_1)+c_{31}\{(1-x_1)(x_3-2x_1)-x_3x_1\}+$$
$$d_{31}\{(1-x_1)(x_3-3x_1)-2x_3x_1\}(x_3-x_1)+\ldots]+$$
$$x_2x_3[B(1-2x_1)+C_1(x_2-x_3)(1-3x_1)+$$
$$C_2\{(x_3-x_1)(1-3x_1)-x_1\}+$$
$$C_3\{(x_1-x_2)(1-3x_1)+x_1\}+\ldots] \qquad (16)$$

Similar equations for $\log \gamma_2/\gamma_3$; $\log \gamma_3/\gamma_1$; and $\log \gamma_2$, $\log \gamma_3$ are given by use of cyclic permutation $1 \rightarrow 2 \rightarrow 3 \rightarrow 1$ for subscripts in Equations (15) and (16).

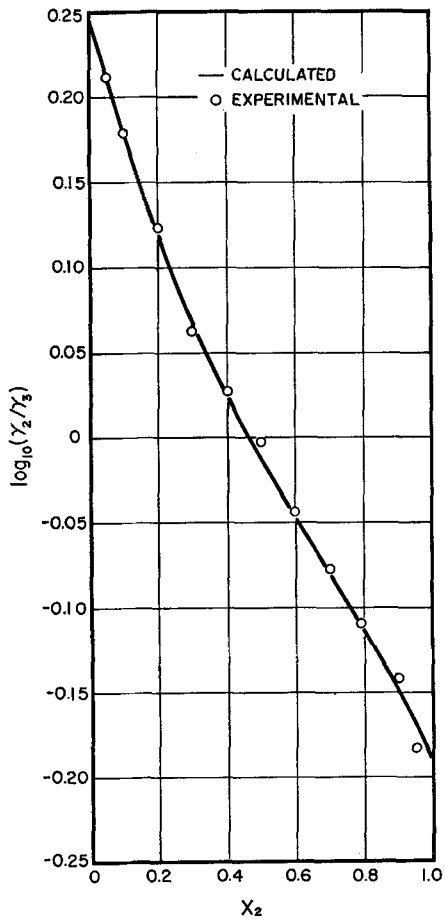

Fig. 3. Redlich-Kister plot for the system *n*-heptane(2)-toluene(3).

RESULTS

Experimental data for the three binary systems are presented in Table 2. Figure 3 shows the logarithm of the ratio of activity coefficients plotted against the composition for the *n*-heptane-toluene system. Figure 3 also shows the calculated curve of the form of Equation (10), using the constants for the system shown in Table 4. Similar figures were obtained for the two other binary systems. The binary constants b_{ij}, c_{ij}, and d_{ij} shown in Table 4 were determined by a curve fit of the data for each system. Since the calculated curves automatically satisfy Equation (7), it can be seen that the thermodynamic consistency of the data is very good.

Deviations from ideality were positive in all cases but were very small for the aliphatic system cyclohexane-*n*-heptane. Maximum activity coefficients in this case were 1.11 for cyclohexane and 1.16 for *n*-heptane. Much larger deviations were observed for the mixed aliphatic-aromatic systems, cyclohexane–toluene and *n*-heptane–toluene, with maximum activity coefficients of about 1.6 to 1.8 for each constituent in both systems.

Experimental data for the ternary system are given in Table 3, and the sixteen ternary compositions indicated in Figure 5 were chosen so that they are evenly distributed on a triangular composition diagram. These compositions of the mixtures were always prepared within a mole

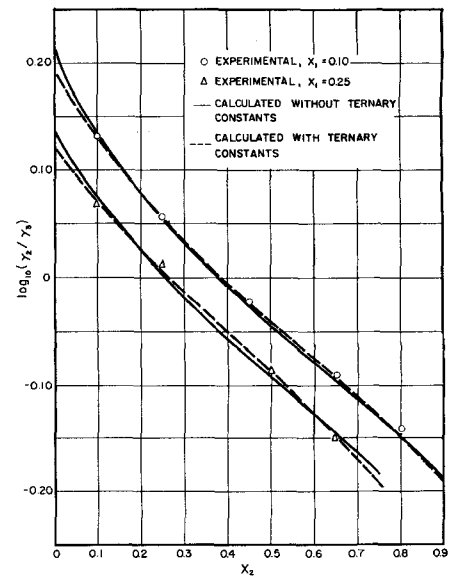

Fig. 4. Redlich-Kister plot for ternary system, cyclohexane(1)-*n*-heptane(2)-toluene(3), at constant concentrations of cyclohexane.

fraction of 0.0016 of the desired values. Experimental values of log γ_2/γ_3 at constant concentrations of cyclohexane ($x_1 = 0.10$ and $x_1 = 0.25$) are shown in Figure 4 along with the correlations obtained by the Redlich Kister method. The ternary constants B, C_1, C_2, and C_3 used for these correlations were obtained by a least squares analysis of the forty-eight experimental log γ_i/γ_j with an IBM 1620 computer. The ternary constants are shown in Table 4. Correlations were made with and without the use of the ternary constants and the correlations for the both cases are shown in Figure 4. Figures similar to Figure 4 were obtained for the cases of constant concentrations of *n*-heptane and of toluene. The average deviation of the experimental values from the correlating equation for sixteen points was 1.71% when best values of all the constants were used and 1.77% when the ternary constants were set to zero. Since maximum deviation was also about the same with and without use of the ternary constants, their use is not indicated. It should be noted that the calculated curves satisfy the consistency requirement, Equation (6), whether or not ternary constants are used. Experimental errors are slightly greater than for the binary compositions, but the comparisons of the experimental log γ_i/γ_j with the correlating equation again indicated thermodynamic consistency within experimental error. It should be noted, however, that the test by Equation (6) could be done twice for twelve points and once for three points (where $x_i = 0.10$ and $x_j = x_k$), but not at all for the center point.

Activity contours for each species are also shown in Figures 5 and 6, as calculated from Equation (16). These contours were calculated without use of the ternary constants, and are therefore obtainable solely from binary data.

DISCUSSION

The accuracy obtained in these experiments compares favorably with reported results for similar systems. Mean deviation of the γ_i/γ_j from correlations used was 1.2% for binary systems, and 1.7% for ternary compositions, and accuracy was only slightly less for species present in small amounts. This precision appears better than that reported for the same systems at the normal boiling point (*6, 8* to *10*), and the thermodynamic consistency was clearly superior. Deviations were least for the aliphatic system cyclohexane–*n*-heptane: 0.9% for cyclohexane–*n*-heptane, and 1.4% for both cyclohexane–toluent and *n*-heptane–toluene. This is because reproducibility of the toluene peak on the voltage time curve from the chromatograph was slightly poorer than the reproducibility of the cyclohexane and *n*-heptane peaks, apparently because toluene was the most strongly adsorbed.

Almost all the errors observed occurred in the analysis, and it is felt that they could be reduced substantially. Greatest improvement could be obtained by use of a chromatograph with better facilities for controlling column temperature and carrier gas flow rate. A greater separation of the peaks for the three organic constituents would have been desirable, and this could best be obtained by use of a more selective adsorbent. Better separation can also be obtained by lowering operating temperature and gas flow rate, but these changes give poorer reproducibility.

On balance the technique used was satisfactory and offered a number of substantial advantages: (1) The static equilibration method is simpler and is less subject to error than the dynamic methods (*4*). (2) The still is of simple construction and does not require specialized operating techniques (*16*). (3) Liquid compositions can be set accurately for convenience in data correlation. (4) Multicomponent solutions can be analyzed nearly as simply as binaries. (5) It is especially suitable for systems of limited solubility or undesirable physical properties, for example, partially miscible liquids, salt solutions, and viscous solutions of high polymers. (6) The method is also

TABLE 3. EXPERIMENTAL DATA OF TERNARY SYSTEM AT 25°C.

Cyclohexane(1)-*n*-heptane(2)-toluene(3)

Composition, mole fraction		Partial pressure, mm. Hg				
x_1	x_2	p_1	p_2	p_3	$\log_{10}(\gamma_1/\gamma_2)$	$\log_{10}(\gamma_2/\gamma_3)$
0.1010	0.1001	13.09	6.318	23.20	—0.0167	0.1312
0.1009	0.2505	12.18	14.14	20.02	0.0006	0.0562
0.1001	0.4494	11.26	22.85	15.01	0.0155	—0.0227
0.1003	0.6492	10.86	30.99	9.166	0.0265	—0.0907
0.1007	0.7990	10.63	36.29	3.927	0.0370	—0.1414
0.2499	0.1005	29.92	5.871	20.21	—0.0179	0.0678
0.2510	0.2493	27.88	12.75	15.46	0.0075	0.0124
0.2509	0.4986	26.45	23.46	8.968	0.0213	—0.0873
0.2510	0.6489	25.96	29.37	3.990	0.0295	—0.1507
0.3335	0.3325	34.90	16.00	11.24	0.0081	—0.0509
0.4495	0.0999	49.02	5.340	15.15	—0.0195	—0.0048
0.4502	0.4484	46.12	21.77	4.240	—0.0050	—0.1412
0.5001	0.2500	51.48	12.25	9.207	—0.0070	—0.0779
0.6502	0.0996	67.91	5.282	9.907	—0.0351	—0.0790
0.6493	0.2501	65.25	12.34	4.268	—0.0202	—0.1407
0.7992	0.0997	79.24	5.243	4.505	—0.0539	—0.1339

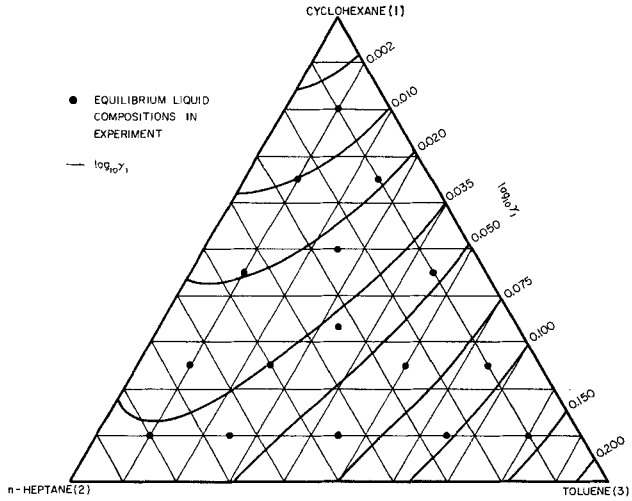

Fig. 5. Contour curves of log γ_3 and data points.

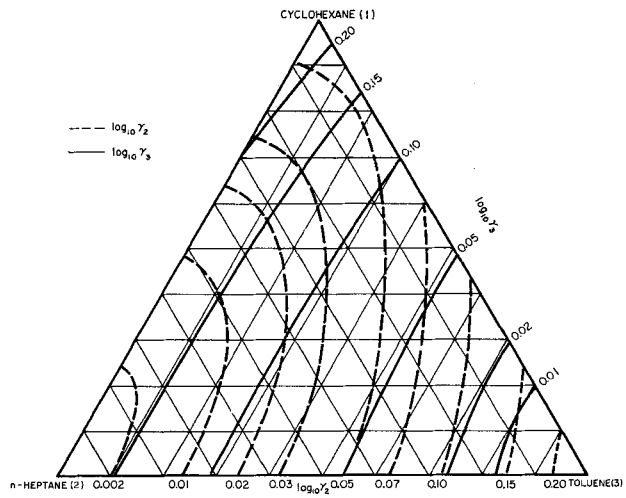

Fig. 6. Contour curves of log γ_2 and log γ_3.

TABLE 4. CONSTANTS OF REDLICH-KISTER EQUATION

The system cyclohexane(1)-*n*-heptane(2)-toluene(3) at 25°C.

Binary constants			Ternary constants
$b_{12} = 0.05485$	$c_{12} = 0.01068$	$d_{12} = 0$	$B = -0.001556$
$b_{23} = 0.19882$	$c_{23} = -0.02838$	$d_{23} = 0.02076$	$C_1 = 0.064727$
$b_{31} = 0.21098$	$c_{31} = 0$	$d_{31} = 0.01963$	$C_2 = -0.064054$
			$C_3 = 0.025714$

especially suitable for isothermal measurements and at low vapor pressures. (7) Only very small vapor samples are required in principle so that adaptation to semimicro-scale operation is possible (*15*).

It is interesting to note that ternary behavior was predictable with satisfactory accuracy from binary data. This possibility was suggested earlier by Black (*2*), who found it suitable for a number of systems showing moderate departures from ideality. For our purposes, however, the Redlich-Kister correlation used in this work is preferable to the modified Van Laar equations suggested by Black. This is because ratios of activity coefficients were more accurately known than the coefficients themselves, as discussed above.

Efforts to predict the behavior of this system at 25°C., either a priori or from data at the normal boiling point, were only partially successful.

Comparisons of extrapolated experimental activity coefficients with regular solution theory were made for infinite dilution of these binary systems. The theoretical values were calculated from the binary expression

$$\left[\log \gamma_i = \frac{V_i}{2.3\,RT} (\delta_i - \delta_j)^2 \right]_{x_j=1} \qquad (17)$$

Values of the parameters V_i and δ_i at 25°C. were taken from the table of Hildebrand and Scott (*5*).

Reasonable agreement was obtained for cyclohexane–*n*-heptane and *n*-heptane–toluene, but not for cyclohexane–toluene. Results for the nearly ideal aliphatic cyclohexane–*n*-heptane system are to be expected, but agreement for the aliphatic-aromatic *n*-heptane–toluene mixture is probably fortuitous. Discrepancies observed for the cyclohexane–toluene system are to be expected for molecules of such dissimilar character.

Also, comparisons with calculated values of Black (*2*) and extrapolated values of Rettig (*12*) were made. Both calculations are based primarily on Myers' data taken at the normal boiling point (*6, 8, 9*). It may easily be shown from Black's results given for 90° and 105°C. that a linear extrapolation to 25°C. is not successful.

Rettig's extrapolations were made by a modification of regular solution theory and heats of mixing at 25°C. (*13*). He assumed the temperature dependence of the excess molal free energy to be linear. Excess molal free energy ΔF can be expressed in terms of a characteristic parameter w by (7)

$$\Delta F = x_1 x_2 w \qquad (18)$$

This parameter w is related to the molal heat of mixing by

$$(\Delta H)_T = x_1 x_2 \left(w_T - T \frac{\partial w_T}{\partial T} \right) \qquad (19)$$

Rettig estimated w for 25°C. from Equation (19) by use of $\frac{w_T - w_{298}}{T - 298}$ as an approximation for $\frac{\partial w_T}{\partial T}$ and the heat of mixing at 25°C. Values of w at the boiling point T in the term of $\frac{w_T - w_{298}}{T - 298}$ could readily be calculated for each composition from Myers' data and Equation (18). This extrapolation was satisfactory only for the nearly ideal system cyclohexane–*n*-heptane, and it appears therefore that rather complete heat of mixing data are required if accuracy comparable to experimental measurements is desired. On balance it appears preferable to remeasure activities at the desired temperature.

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NOTATION

A = area under the voltage time curve
B, b_{ij}, C_i, c_{ij}, and d_{ij} = constants in the Redlich-Kister equations
F = liquid molal free energy
f = weighting factor
H = liquid molal enthalpy
P_i° = vapor pressure of pure component i
p = pressure
p_i = partial pressure of component i
Q = dimensionless excess free energy
R = gas constant
T = absolute temperature
V = liquid molal volume
w = characteristic parameter defined by Equation (18)
x = mole fraction in liquid phase

γ = liquid activity coefficient
Δ = excess value
δ = solubility parameter

Subscripts

ideal = ideal solution
i, j, k = components
1, 2, 3 = components

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