ACKNOWLEDGMENT

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NOMENCLATURE

$B_{12}B_{23}B_{31}$,
$C_{12}C_{23}C_{31}$,
$D_{12}D_{23}D_{31}$,
$E_{12}E_{23}E_{31}$ = binary constants of the Redlich-Kister equations
$C_1C_2C_3$ = ternary constants of the Redlich-Kister equations
p^0 = vapor pressure of pure component
x = liquid phase mole fraction of component
y = vapor phase mole fraction of component
γ = liquid phase activity coefficient
π = total pressure

Subscripts

$1,2,3,i$ = components

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Liquid-Liquid Equilibria for the System Ethylene Glycol–Toluene–Acetone

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Liquid-liquid equilibrium (tie line) data are presented for the system ethylene glycol-toluene–acetone at 0° and 24° C. Gas chromatography was used in the analysis. The raw data are correlated as smoothed curves, and numerical and graphical comparisons are made between the data and the correlations. The data are internally consistent, both at a given temperature and between temperatures, and agree with previously reported work except for ethylene glycol concentration in the toluene phase.

EFFECT of temperature upon the liquid-liquid equilibria of a nonaqueous ternary system and the suitability of gas chromatographic methods in determining liquid-liquid solubilities and tie line data were investigated.

EXPERIMENTAL

Materials. The acetone (Mallinckrodt N. F. Grade), the toluene (Mallinckrodt A. R. Grade), and the ethylene glycol (Central Scientific Co.) were tested for purity with the gas chromatograph as described below. No impurities were detected at the 0.02% level.

Procedure. The procedure differed from usual determinations of phase equilibria, for instance those discussed by Treybal (*2*), in that only tie line data were obtained. Two-phase mixtures of various compositions were placed in 25-ml. bottles which were closed with aluminum foil-lined plastic caps to minimize evaporation. The two phases in each bottle were of about equal volume to simplify sampling. These bottles, plus two containing known single phase mixtures for purposes of standardizing the chromatograph, were placed in a thermostat and held within 0.5° C. of the desired temperatures, 0° and 24° C. The individual bottles were shaken vigorously twice a day for four days while the system reached thermal and phase equilibrium. The phases were then allowed to separate before they were sampled.

Some comment on the rate of phase separation should be made at this point. The two phases appear to separate rapidly with substantially complete separation in 5 to 10 minutes. In the early part of this investigation, about one hour was allowed between the last (hand) shaking of the samples and their analysis. However, the same samples at the same temperature had less glycol and acetone in the toluene layer if a day or so were allowed for the phases to separate.

Since temperature control offered no problem, phase separation was assured by keeping the equilibrated samples thermostated, closed, and undisturbed for six days prior to running the analyses.

Analysis. The samples were analyzed by gas chromatography using an Aerograph Model A-90-P gas chromatograph connected to a Honeywell ElectroniK 18 recorder. The column consisted of a 10-foot by ¼-inch stainless steel tube packed with 40% carbowax 20M on Chromosorb W. The column temperature was 210° C., the injector block temperature was 270° C., and the (thermal conductivity) detector temperature was 250° C. Helium, flowing at 25 cc. per minute, was used as a carrier gas. Residence times for the compounds were about 2.25 minutes for acetone, 3.0 minutes for toluene, and 8.5 minutes for ethylene glycol.

Samples for analysis were taken directly from the sample bottles using a Hamilton 10-μl. syringe. The needle was inserted in the layer to be sampled, pumped five or six times to eliminate any residual material in the syringe, and

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filled to 5 to 6 µl. After filling, the syringe was removed from the bottle and the syringe needle wiped before the sample size was adjusted to 1 µl. The needle tip was then touched to clean glass to remove any drop, and the 1 µl. sample was injected into the chromatograph.

The chromatograph trace was converted to mole fractions of the individual components by using the fact that peak height is proportional to peak area for a given component provided that peak width remains constant. This criterion may be met if small samples are used to avoid flooding the column and provided the chromatographic conditions (injector, column, and detector temperature, helium flow rate, and detector current) are held constant. The factors for converting the peak height of the individual components to the moles of the individual components present—more precisely, to three numbers proportional to the moles of the individual components present—were obtained by analyzing single phase mixtures of known compositions each day analyses were run. Two such mixtures were used. One, of approximately 47 (mole)% ethylene glycol, 8% toluene, and 45% acetone, was used to obtain constants for analyzing the ethylene glycol layer, and the other, approximately 6% ethylene glycol, 30% toluene, and 64% acetone, was used to obtain the constants for analyzing the toluene layer. A similar method of analysis has been reported by Kabel and Johanson (*1*).

DATA

The experimental data are presented in terms of mole fractions in the first six columns of Table I. In the case of acetone and toluene, the error in the analyses is no more than ±0.0002 or 1% of the amount present, whichever is greater; in the case of ethylene glycol, ±0.001 or 1% of the amount present. Since these data represent tie line data, they may be tested using an Othmer-Tobias plot of

$$\frac{1\text{-}X_{AA}}{X_{AA}}\ vs.\ \frac{1\text{-}X_{BB}}{X_{BB}}$$

as shown in Figure 1. All data, except that for phases containing less than 0.5% acetone, are included. The reason for excluding data at the lowest acetone concentrations is that the test increases in sensitivity as the concentration of the miscible component decreases. In this particular system, the test becomes erratic at low concentrations of acetone. As an example, at 0% acetone an error of 0.001 in the analysis of glycol in toluene at 24° C. would result in a 50% error in the value of

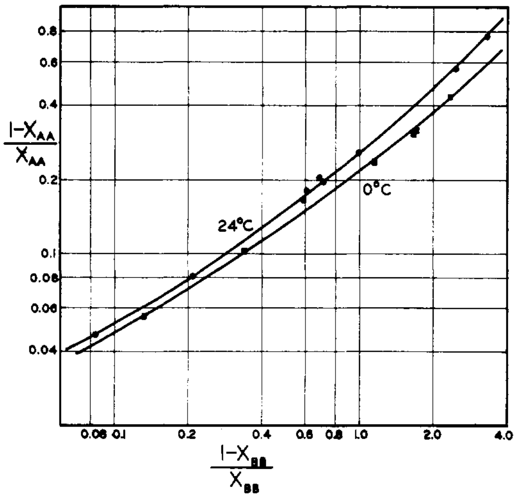

Figure 1. Othmer-Tobias plot

$$\frac{1\text{-}X_{BB}}{X_{BB}}$$

As may be seen, the data fall on two smooth lines, both of which have a slight but definite curvature.

The individual values for the smoothed data presented in columns 7 through 12 of Table I were obtained as follows:

X_{CA} was chosen arbitrarily but near an experimental value
X_{BA} was obtained from a plot of X_{BA} *vs.* X_{CA}
X_{CB} was obtained from a plot of X_{CB} *vs.* X_{CA}
X_{AB} was obtained from a plot of X_{AB} *vs.* X_{CB}
X_{AA} was caluclated as $1\text{-}X_{BA} - X_{CA}$
X_{BB} was calculated as $1\text{-}X_{AB} - X_{CB}$

A comparison of the raw data and the smoothed data is presented in Figures 2 and 3 in which the round points represent the raw data and the lines represent the smoothed data. The dashed lines are extrapolations and the points labeled *P* are estimated plait points.

Table I. Liquid-Liquid Equilibrium for the System Ethylene Glycol–Toluene–Acetone
(All figures in terms of mole fractions)

Actual Data						Smoothed Data					
Ethylene glycol phase			Toluene phase			Ethylene glycol phase			Toluene phase		
X_{AA}	X_{BA}	X_{CA}	X_{AB}	X_{BB}	X_{CB}	X_{AA}	X_{BA}	X_{CA}	X_{AB}	X_{BB}	X_{CB}
0° C.						0° C.					
0.981	0.0166	0.0025	0.0005	0.995	0.0042	0.9834	0.0166	0.0000	0.0005	0.9995	0.0000
0.947	0.0191	0.0335	0.0000	0.883	0.117	0.9491	0.0174	0.0335	0.0013	0.882	0.117
0.908	0.0198	0.0726	0.0047	0.748	0.248	0.9077	0.0198	0.0725	0.005	0.747	0.248
0.808	0.0302	0.1622	0.0409	0.467	0.493	0.8080	0.0295	0.1625	0.0425	0.4625	0.495
0.764	0.0356	0.201	0.0756	0.376	0.549	0.7647	0.0353	0.2000	0.075	0.376	0.549
0.759	0.0356	0.206	0.0749	0.370	0.555						
0.697	0.0453	0.258	0.1192	0.301	0.580	0.6972	0.0453	0.2575	0.119	0.301	0.580
			Estimated Plait Point			0.45	0.10	0.45			
24° C.						24° C.					
0.979	0.0199	0.0010	0.0021	0.995	0.0032	0.9802	0.0198	0.0000	0.002	0.998	0.0000
0.956	0.0210	0.0235	0.0052	0.923	0.0721	0.9555	0.0210	0.0235	0.0032	0.925	0.072
0.925	0.0219	0.0531	0.0076	0.827	0.1660	0.9238	0.0232	0.0530	0.0078	0.831	0.161
0.858	0.0317	0.1107	0.0284	0.629	0.342	0.8593	0.0297	0.1110	0.0246	0.653	0.322
0.847	0.0307	0.1218	0.0283	0.620	0.352						
0.835	0.0316	0.1330	0.0360	0.585	0.380						
0.830	0.0351	0.1348	0.0351	0.594	0.371	0.8316	0.0334	0.1350	0.0370	0.582	0.381
0.796	0.0388	0.1656	0.0587	0.502	0.439	0.7956	0.0389	0.1655	0.0587	0.499	0.442
0.639	0.0721	0.289	0.1802	0.288	0.532	0.6387	0.0723	0.289	0.180	0.290	0.530
0.567	0.0936	0.339	0.257	0.233	0.510	0.5673	0.0937	0.339	0.257	0.232	0.511
			Estimated Plait Point			0.42	0.145	0.435			

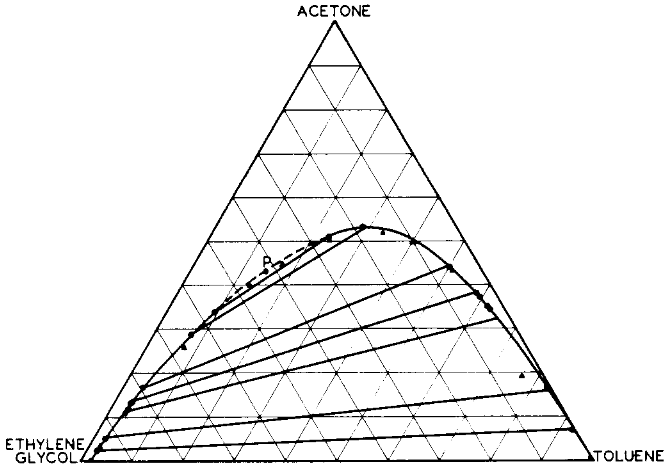

Figure 2. Liquid-liquid equilibrium at 0° C. for the system ethylene glycol–toluene–acetone

Points, raw data; lines, smoothed data; mole basis

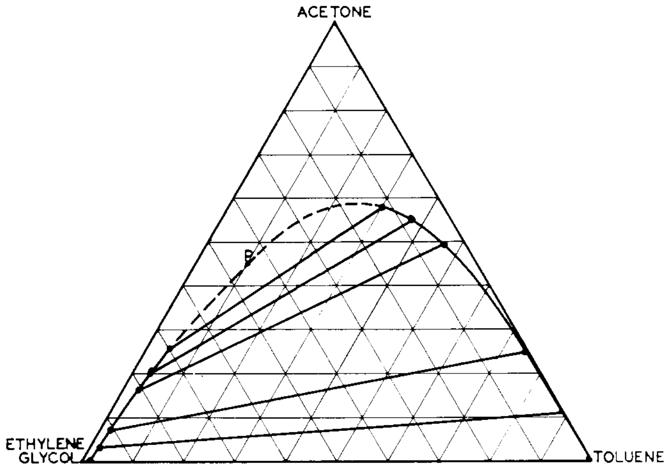

Figure 3. Liquid-liquid equilibrium at 24° C. for the system ethylene glycol–toluene–acetone

Circles, raw data; lines, smoothed data; triangles, Trimble and Frazer at 27° C.—all on mole basis

Comparison with Previous Work. The only previous work reported on this system is that of Trimble and Frazer (*3*) who present phase data and tie line data obtained at 27° C. Representative data from their work are shown as triangles in Figure 3. They made their determinations by turbidimetric procedures and reported their results in terms of volume per cent. Agreement between the two sets of data is good, except for ethylene glycol solubility in toluene at acetone concentrations below 40 mole %. Trimble and Frazer report only one datum point in this area, that of 4.3% ethylene glycol, 76.5% toluene, and 19.1% acetone. Since the phases appear to separate well in 5 to 10 minutes, (a faint blue-gray haze might be claimed) but require a much longer time for the toluene phase to reach a steady analysis, and since the data reported in this work were collected by a method designed to assure complete separation, it would appear that the data reported in this work are true equilibria. It is quite possible that the data of Trimble and Frazer accurately describe the separation which could be obtained in a continuous commercial process.

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Virial Coefficients and Stockmayer Parameters for Propyne

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EXPERIMENTAL *P-V-T* measurements on propyne at temperatures from 50° to 200° C. and at pressures to 315 atm. have been recently performed by Vohra and coworkers using a Beattie-type apparatus (*4*). The data were presented in a graph of compressibility factor *vs.* pressure for various isotherms. While this presentation is useful for many purposes, the data may be better analyzed in the low to moderate pressure regions by plotting $(Z\text{-}1)\,V$ *vs.* $1/V$. This analysis permits the determination of the second and third virial coefficients as well as a check upon the internal consistencies of the data. In this study, such an analysis was carried out for each isotherm.

The resulting values of the second virial coefficients were compared with the Lennard-Jones and the Stockmayer potentials using graphical methods. These graphical procedures allow one to determine whether a given potential fits the data in a single graph. Furthermore, if a fit is found, the parameters of the potential are easily determined from the same graph.

The Lennard-Jones intermolecular potential energy function is as follows:

$$\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^{6}] \qquad (1)$$

in which r is the distance between interacting chemical