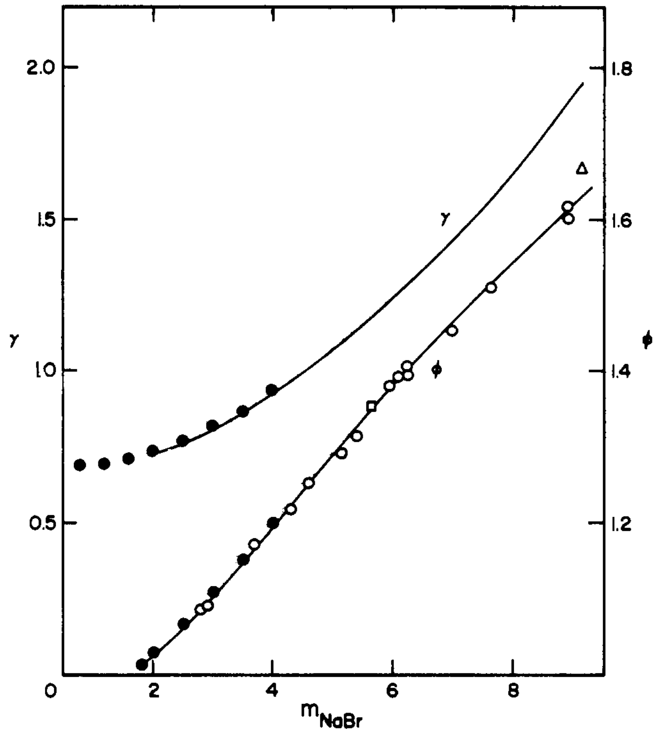

Figure 1. Activity coefficients (left hand scale) and osmotic coefficients (right hand scale) of sodium bromide solutions

○ This work

□ This work, 26° C.

△ Saturated solution data (2, 8)

● Data of Robinson and Stokes (7)

and activity coefficients for round values of m, calculated from Equations 2 and 4, are shown in Table II.

DISCUSSION

The solubility of sodium bromide in water at 25° is reported (*8*) to be 48.61 grams of NaBr in 100 grams of saturated solution (the solid phase is $NaBr \cdot 2H_2O$), which corresponds to a molality of 9.190. This value may be combined with the reported (*6*) values of the activity of water in the saturated solution, $a_W = 0.577$, to give the value for the osmotic coefficient $\phi = -\ln a_W/0.01802\ \nu m = 1.660$. The value calculated from Equation 2 is 1.639 for this molality, about 1.5% too low, which is acceptable since reported solubility is an average of values ranging about 0.8% on either side (*8*).

Table II. Osmotic and Activity Coefficients for NaBr, 25°

	ϕ		γ	
m	Ref. 7, p. 468	This work	Ref. 7, p. 477	This work
0.5	0.933	...	0.697	...
1.0	0.958	...	0.687	...
1.5	0.990	...	0.702	...
2.0	1.028	1.023	0.731	0.729
2.5	1.067	1.057	0.768	0.761
3.0	1.107	1.097	0.812	0.804
3.5	1.150	1.144	0.865	0.857
4.0	1.199	1.192	0.929	0.919
4.5	...	1.240	...	0.992
5.0	...	1.287	...	1.062
5.5	...	1.337	...	1.174
6.0	...	1.382	...	1.240
6.5	...	1.426	...	1.338
7.0	...	1.465	...	1.442
7.5	...	1.503	...	1.552
8.0	...	1.538	...	1.658
8.5	...	1.579	...	1.760
9.0	...	1.615	...	1.910

The activity coefficients of sodium bromide at high concentrations fall neatly between those of the chloride and the iodide (*3*), and are somewhat higher than those of the thiocyanate (*3*). The general conclusion is, according to Miller and Sheridan (*3*), that the behavior of sodium bromide in concentrated solutions is an extension of its behavior at low concentrations, and shows nothing unexpected.

NOMENCLATURE

a_W = activity of water, mole fraction scale
m = molality, moles per 1000 grams of water
γ = mean ionic stoichiometric activity coefficient, molal scale
ϕ = osmotic coefficient, molal scale
ν = number of ions into which an electrolyte dissociates

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Vapor-Liquid Equilibrium Data

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EXPERIMENTAL vapor-liquid equilibrium data are important for chemical engineers in considering separation factors of mixtures from an industrial and theoretical standpoint.

This paper presents equilibrium data for binary and ternary mixtures including 2-propanol, and the relation between the ternary and the binary data is analyzed thermodynamically using the Redlich-Kister equations.

EXPERIMENTAL

Binary vapor-liquid equilibrium data at 500 mm. of Hg were determined for the 2-propanol–hydrocarbon mixtures,

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Vapor-liquid equilibrium data are presented for the three binary systems: benzene–2-propanol, cyclohexane–2-propanol, and 2-propanol–methylcyclohexane at 500 mm. of Hg; for the binary carbon tetrachloride–2-propanol system and for the ternary carbon tetrachloride–benzene–2-propanol system at 760 mm. of Hg.

mixtures of 2-propanol, benzene, cyclohexane, and methylcyclohexane using a modified Gillespie type of still. Each binary system forms an azeotropic mixture. The thermodynamic consistency of the binary data was checked using the four-constant, Redlich-Kister (*5*) equations.

Materials. Reagent grade cyclohexane and methylcyclohexane were used directly. Benzene, C. P. grade, was purified by recrystallization. 2-Propanol, C. P. grade, was treated with anhydrous copper sulfate to remove water and distilled through a laboratory fractionating column packed with McMahon packings. Only the middle cuts were used for experimental work. In Table I, the physical properties of chemicals used are compared with the literature values.

Analysis. Fifteen mixtures of known composition were prepared at approximately equal intervals of composition. Refractive index of the mixtures was read at 25° C. by means of an Atago-Abbe refractometer with an accuracy of 0.002 to make a calibration chart for each binary system. Uncertainty in observed composition was ±0.001 mole fraction.

Apparatus. The original Gillespie still has been modified and improved by many investigators. The equilibrium still described in Figure 1 was used for obtaining equilibrium data. It was a combination of the equipment used by Scatchard and Ticknor (*6*) and by Smit and Ruyter (*7*). Temperature measurements were made by using a Yokogawa P-7 potentiometer connected with a galvanometer and a copper-constantan thermocouple with an accuracy of ±0.05° C. A Cartesian manostat was used to maintain the total pressure in the still at 500 mm. of Hg with a maximum deviation of ±1 mm. of Hg. Observed temperatures were corrected to 500 mm. of Hg using the Clausius-Clapeyron equation.

Table I. Physical Properties of the Chemicals Used (9)

Chemical	Normal Boiling Point, ° C. Exptl.	Normal Boiling Point, ° C. Lit.	Refractive Index, 25° C. Exptl.	Refractive Index, 25° C. Lit.
Benzene	80.10	80.103	1.4980	1.49790
Carbon tetrachloride	76.70	76.75	1.4573	1.45759
Cyclohexane	80.73	80.738	1.4237	1.42354
Methylcyclohexane	100.92	100.934	1.4210	1.42058
2-Propanol	82.39	82.40	1.3747	1.3747

RESULTS AND THERMODYNAMIC ANALYSIS

The experimental data for the three binary systems are reported in Table II. Observed azeotropic compositions and temperatures at 500 mm. of Hg are as follows:

	Mole Fraction of 2-Propanol	Temp., ° C.
Benzene–2-propanol	0.349	60.1
Cyclohexane–2-propanol	0.360	57.8
2-Propanol–methylcyclohexane	0.604	66.5

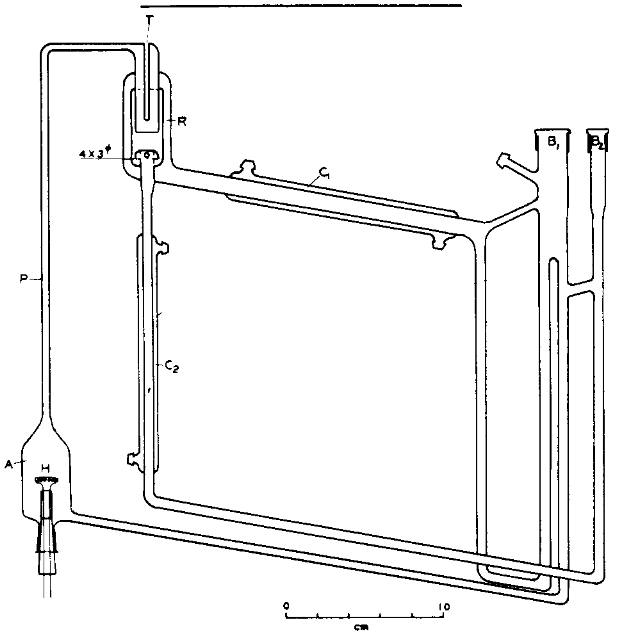

Figure 1. Modified Gillespie still

A, boiling flask; B₁B₂, sampling openings; C₁C₂, coolers; H, internal heaters; P, Cottrel pump; R, disengagement chamber; T, thermometer well

Table II. Experimental Equilibrium Data for the Binary Systems at 500 mm. of Hg Pressure

Benzene–2-Propanol					Cyclohexane–2-Propanol					2-Propanol–Methylcyclohexane				
t, ° C.	x_1^a	y_1	γ_1	γ_2	t, ° C.	x_1^b	y_1	γ_1	γ_2	t, ° C.	x_1^c	y_1	γ_1	γ_2
69.5	0.039	0.148	3.488	1.005	67.3	0.029	0.132	4.238	1.000	75.4	0.030	0.344	9.954	0.972
67.1	0.089	0.262	2.932	1.010	67.0	0.068	0.253	3.781	1.012	71.0	0.077	0.434	5.921	1.022
65.4	0.142	0.350	2.611	1.024	63.1	0.138	0.394	3.297	1.056	64.8	0.180	0.491	3.150	1.112
63.9	0.197	0.424	2.402	1.040	61.2	0.213	0.476	2.759	1.092	68.0	0.250	0.511	2.457	1.207
62.9	0.255	0.469	2.124	1.080	60.1	0.266	0.517	2.492	1.131	67.0	0.331	0.540	2.050	1.317
61.8	0.335	0.525	1.884	1.141	59.1	0.313	0.538	2.280	1.210	66.8	0.427	0.558	1.654	1.489
61.0	0.414	0.563	1.675	1.231	58.3	0.408	0.578	1.930	1.335	66.7	0.509	0.581	1.456	1.654
60.9	0.495	0.600	1.500	1.316	58.0	0.475	0.598	1.734	1.456	66.6	0.581	0.600	1.321	1.850
60.3	0.566	0.626	1.400	1.476	57.8	0.556	0.619	1.546	1.650	66.5	0.668	0.623	1.196	2.209
60.2	0.640	0.647	1.283	1.685	57.8	0.637	0.632	1.374	1.942	66.5	0.735	0.650	1.134	2.570
60.1	0.716	0.674	1.198	1.979	57.9	0.734	0.664	1.253	2.411	67.0	0.788	0.682	1.085	2.863
60.3	0.797	0.707	1.120	2.463	58.5	0.818	0.687	1.138	3.197	67.5	0.843	0.719	1.048	3.364
63.0	0.942	0.828	1.010	4.466	59.1	0.884	0.713	1.070	4.466	68.1	0.887	0.768	1.036	3.774
64.7	0.976	0.896	0.998	6.069	61.9	0.963	0.816	1.021	7.894	69.2	0.935	0.835	1.017	4.501
										70.3	0.965	0.899	1.010	4.924

[a] Mole fraction of benzene. [b] Mole fraction of cyclohexane. [c] Mole fraction fraction of 2-propanol.

Experimental activity coefficients for the components were calculated using the following equation neglecting vapor phase imperfection.

$$\gamma_i = \frac{\pi y_i}{P_i^0 x_i} \tag{1}$$

The vapor pressure data for the pure components were taken from the literature values (*1, 2*). The experimental values of log γ_1/γ_2 *vs.* compositions shown in Figures 2, 3, and 4 were correlated with the four-constant, Redlich-Kister equations. Although the so-called area equality test is valid at constant temperature, in many isobaric systems the method is applicable for narrow-boiling range systems such as the present ones. Since the data are well correlated with the equations, the present experimental data seem to be thermodynamically consistent.

$$\log \gamma_1 = x_2^2[B + C(3x_1 - x_2) + D(x_1 - x_2)(5x_1 - x_2) + E(x_1 - x_2)^2(7x_1 - x_2)] \tag{2}$$

$$\log \gamma_2 = x_1^2[B + C(x_1 - 3x_2) + D(x_1 - x_2)(x_1 - 5x_2) + E(x_1 - x_2)^2(x_1 - 7x_2)] \tag{3}$$

Table III presents the values of constants of the Redlich-Kister equations.

Vapor-liquid equilibrium data for the carbon tetrachloride-2-propanol and the carbon tetrachloride-benzene-2-propanol systems were determined using a Colburn still. The Redlich-Kister equations were used to analyze experimental data.

MATERIALS

Carbon tetrachloride, C.P. grade, was treated with three successive portions of 100 ml. each of alcoholic sodium hydroxide to remove carbon disulfide; it was then washed several times with water, dried with anhydrous potassium carbonate, and distilled. Benzene, C.P. grade, was subjected to recrystallization. 2-Propanol C.P., was distilled twice after overnight storage over copper anhydride. The physical properties of these purified chemicals are given in Table I.

The Colburn still was used, and the experimental technique in this study was similar to the method described above. The binary mixtures were analyzed by using an Atago-Abbe refractometer at 25° C. Refractive indices and densities of ternary mixtures of known composition were measured over the entire composition range to construct a ternary analytical chart consisting of constant values for each physical property. An intersection between the isometric lines gives the composition of an unknown sample since its refractive index and specific gravity had been determined.

Density was measured at 25° C. in a pycnometer with a Shimadzu balance which could be read to 0.1 mg. The precision with which compositions were determined is ±0.001 mole fraction for the binary mixtures and ±0.002 mole fraction for the ternary mixtures. Maximum atmospheric pressure deviations from 760 mm. of Hg during experimental runs were +6 and −8 mm. of Hg. Measured boiling temperatures were corrected to 760 mm. of Hg using the Clausius-Clapeyron equation.

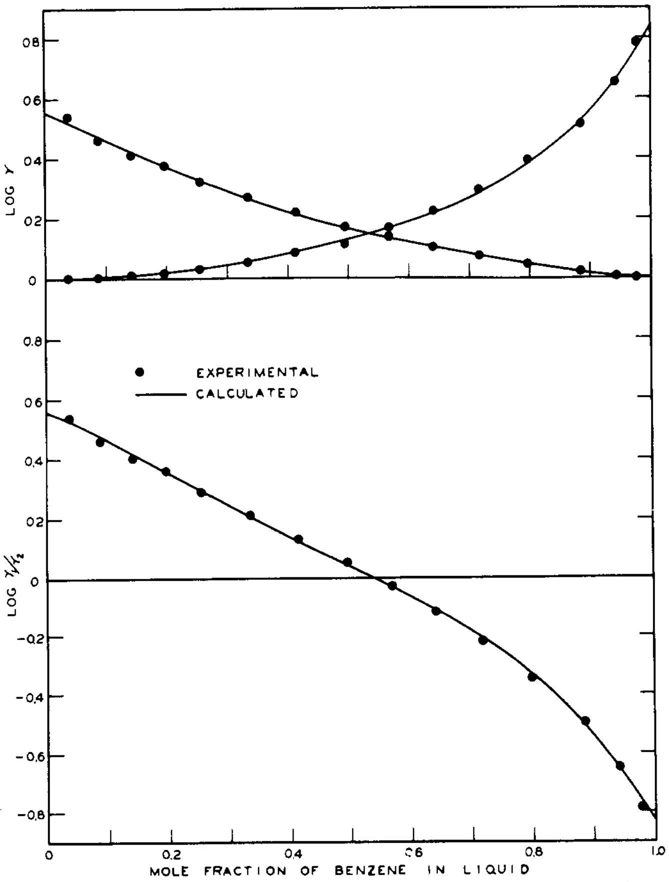

Figure 2. Activity coefficients for the benzene-2-propanol system at 500 mm. of Hg

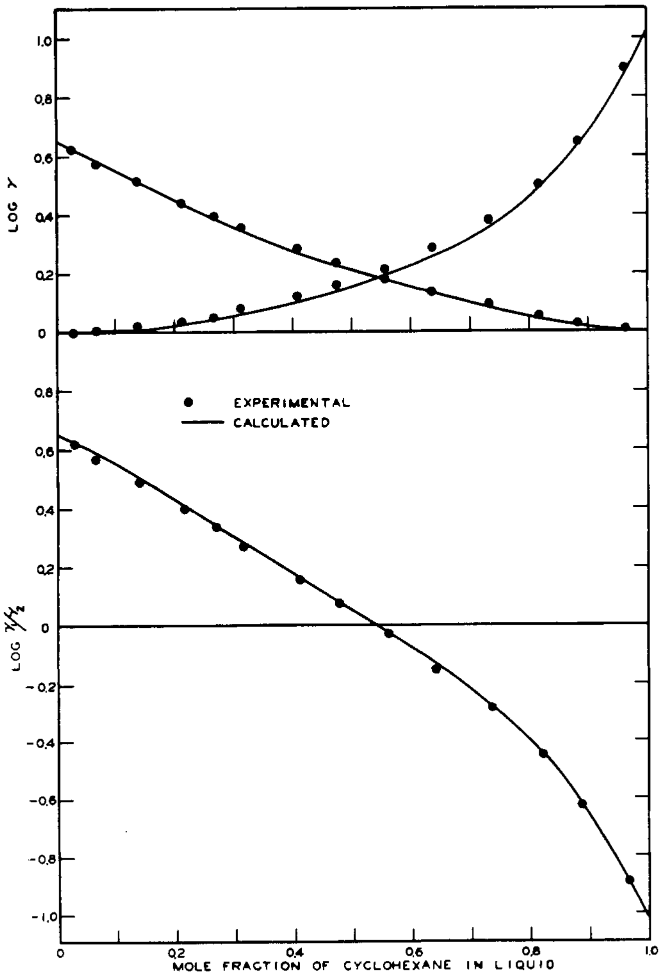

Figure 3. Activity coefficients for the cyclohexane-2-propanol system at 500 mm. of Hg

Table III. Constants of Redlich-Kister Equations for Three Binary Systems at 500 mm. of Hg

Systems	*B*	*C*	*D*	*E*
Benzene–2-propanol	0.6002	0.0767	0.0979	0.0639
Cyclohexane–2-propanol	0.7260	0.1065	0.1125	0.0801
2-Propanol-methylcyclohexane	0.7613	−0.0907	0.1704	−0.1083

Table IV. Vapor-Liquid Equilibrium Data for the System Carbon Tetrachloride–2-Propanol at 760 mm. of Hg

Temp., ° C.	x_1[a]	y_1	γ_1	γ_2
79.9	0.034	0.114	3.050	1.008
78.5	0.062	0.185	2.831	1.011
76.8	0.092	0.252	2.729	1.026
74.0	0.173	0.376	2.366	1.059
72.8	0.224	0.442	2.222	1.062
70.6	0.342	0.534	1.891	1.164
69.7	0.412	0.575	1.740	1.227
69.1	0.486	0.604	1.575	1.334
69.0	0.578	0.640	1.410	1.489
68.8	0.647	0.665	1.315	1.668
68.9	0.730	0.692	1.212	2.005
69.1	0.804	0.719	1.115	2.487
70.2	0.880	0.760	1.058	3.312
72.2	0.943	0.821	1.002	4.761
74.1	0.970	0.893	0.999	4.986

[a] Mole fraction of carbon tetrachloride.

EQUILIBRIUM DATA

Observed equilibrium data for the binary carbon tetrachloride–2-propanol system are listed in Table IV. The present data differ somewhat from those recently reported by Yuan and Lu (*10*) at the middle concentration range (Figure 5). The boiling temperatures over these concentration ranges are close to 70° C. Papousěk, Papoušková, and Págo (*4*) presented the equilibrium data for the carbon tetrachloride–2-propanol system at 70° C. A comparison of the present data with those of Papousěk, Papoušková, and Págo over the concentration range in question yields good agreement. Vapor-liquid equilibrium data for the other binary systems, carbon tetrachloride–benzene and benzene–2-propanol, are available in the literature (*3, 8*). The vapor pressure data for carbon tetrachloride were taken from Weissberger and others (*9*). The three-constant, Redlich-Kister equations were used to correlate the equilibrium data

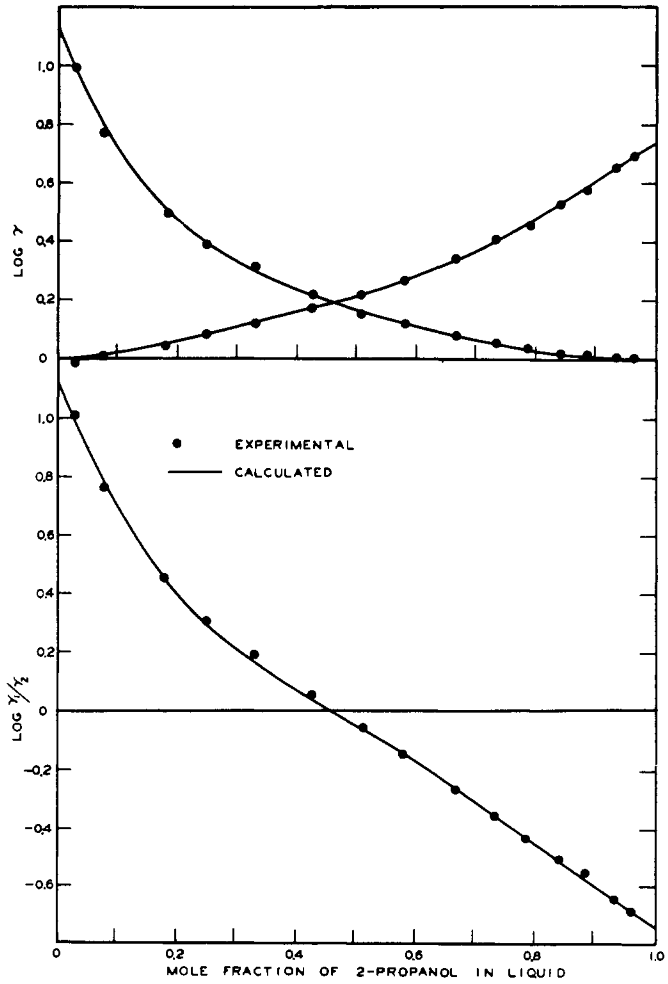

Figure 4. Activity coefficients for the 2-propanol–methylcyclohexane system at 500 mm. of Hg

Table V. Constants of Redlich-Kister Equations for the System Carbon Tetrachloride (1)–Benzene (2)–2-Propanol (3) at 760 mm. of Hg

	Binary Constants	
$B_{12} = 0.0438$	$C_{12} = -0.0101$	$D_{12} = -0.0023$
$B_{23} = 0.5365$	$C_{23} = 0.0813$	$D_{23} = 0.0372$
$B_{31} = 0.5761$	$C_{31} = -0.1166$	$D_{31} = 0.0640$
	Ternary Constants	
$C_1 = 0.2672$	$C_2 = 0.2509$	$C_3 = 0.7264$

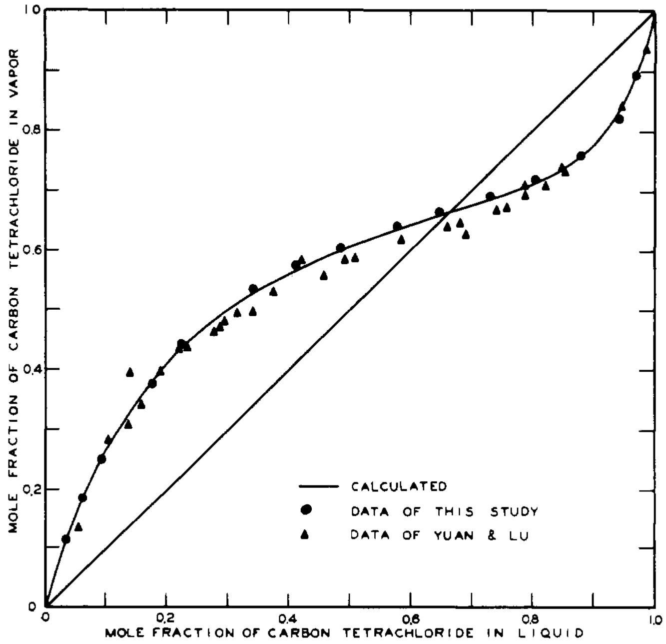

Figure 5. Binary x-y plot for the carbon tetrachloride–2-propanol system at 760 mm. of Hg

Table VI. Experimental Equilibrium Data for the Ternary System Carbon Tetrachloride (1)–Benzene(2)–2-Propanol(3)

Liquid Compn.			Vapor Compn.			Temp., ° C.	Activity Coeff.		
x_1	x_2	x_3	y_1	y_2	y_3		γ_1	γ_2	γ_3
0.032	0.362	0.606	0.054	0.470	0.476	73.5	1.868	1.597	1.128
0.034	0.456	0.510	0.048	0.512	0.440	71.9	1.643	1.453	1.330
0.071	0.430	0.499	0.100	0.472	0.428	72.0	1.636	1.414	1.313
0.371	0.052	0.577	0.508	0.066	0.426	70.2	1.679	1.718	1.223
0.301	0.054	0.645	0.471	0.071	0.458	71.2	1.854	1.747	1.124
0.313	0.083	0.604	0.452	0.111	0.437	71.3	1.713	1.763	1.141
0.429	0.528	0.043	0.416	0.437	0.147	73.8	1.061	1.008	4.868
0.468	0.506	0.026	0.458	0.449	0.093	75.1	1.031	1.038	4.875
0.424	0.555	0.021	0.420	0.487	0.093	75.5	1.029	1.012	5.921
0.092	0.868	0.040	0.100	0.748	0.152	75.9	1.115	0.982	4.921
0.092	0.734	0.174	0.096	0.627	0.277	72.8	1.178	1.072	2.348
0.078	0.621	0.301	0.088	0.563	0.349	71.6	1.325	1.183	1.809
0.058	0.224	0.718	0.112	0.348	0.540	73.5	2.132	1.908	1.076
0.036	0.104	0.860	0.093	0.211	0.696	75.9	2.651	2.313	1.048
0.190	0.651	0.159	0.190	0.545	0.265	71.4	1.176	1.097	2.608
0.169	0.510	0.321	0.186	0.468	0.346	70.9	1.317	1.223	1.727
0.151	0.373	0.476	0.194	0.404	0.402	71.6	1.506	1.410	1.313
0.132	0.238	0.630	0.208	0.322	0.470	71.7	1.845	1.760	1.160
0.106	0.143	0.751	0.203	0.220	0.577	74.6	2.047	1.831	1.054
0.095	0.069	0.836	0.231	0.132	0.637	75.2	2.548	2.229	1.073
0.270	0.664	0.066	0.269	0.550	0.181	73.8	1.091	1.008	3.880
0.275	0.536	0.189	0.270	0.452	0.278	71.2	1.164	1.113	2.324
0.256	0.425	0.319	0.276	0.384	0.340	71.5	1.268	1.184	1.668
0.237	0.280	0.483	0.300	0.304	0.396	71.3	1.501	1.433	1.295
0.203	0.172	0.625	0.315	0.223	0.462	71.3	1.840	1.711	1.168
0.164	0.080	0.756	0.320	0.131	0.549	74.1	2.115	1.973	1.013
0.386	0.552	0.062	0.369	0.456	0.175	73.1	1.070	1.028	4.115
0.358	0.306	0.336	0.380	0.281	0.339	70.1	1.306	1.258	1.680
0.302	0.182	0.516	0.391	0.203	0.406	70.3	1.582	1.517	1.297
0.262	0.090	0.648	0.411	0.126	0.463	72.1	1.810	1.796	1.087
0.490	0.448	0.062	0.459	0.373	0.168	73.5	1.037	1.024	3.891
0.470	0.360	0.170	0.440	0.284	0.276	70.3	1.144	1.073	2.676
0.392	0.213	0.395	0.434	0.209	0.357	70.6	1.340	1.321	1.470
0.601	0.351	0.048	0.552	0.297	0.151	73.0	1.031	1.056	4.609
0.594	0.227	0.179	0.542	0.188	0.260	70.8	1.097	1.108	2.296
0.551	0.101	0.348	0.567	0.103	0.330	69.6	1.285	1.419	1.612
0.713	0.236	0.051	0.641	0.201	0.158	72.8	1.015	1.069	4.573
0.703	0.118	0.179	0.633	0.100	0.267	70.0	1.111	1.165	2.491
0.830	0.125	0.045	0.741	0.106	0.153	73.2	0.996	1.052	4.930

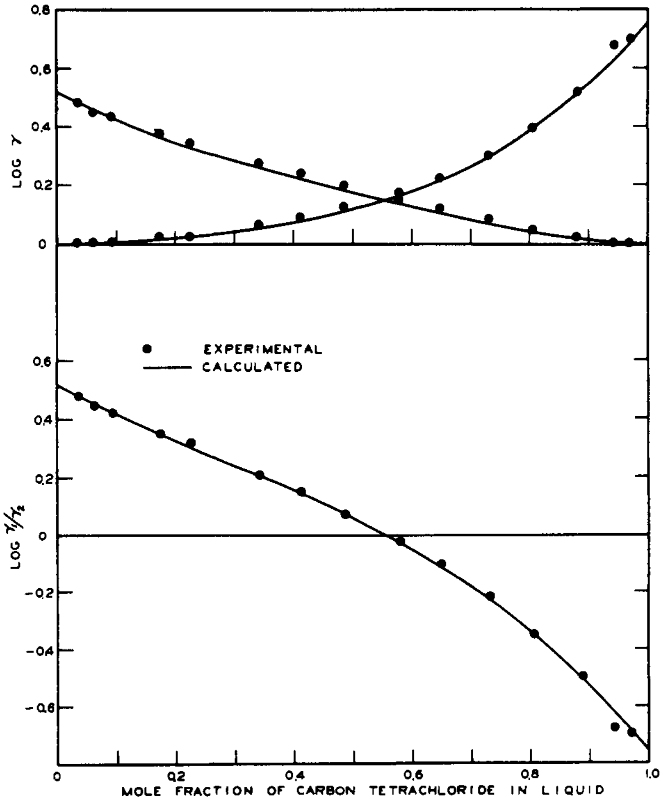

Figure 6. Activity coefficients for the carbon tetrachloride–2-propanol system at 760 mm. of Hg

of the binary systems as described for the first three binary systems. The calculated curve is compared with the experimental values for the carbon tetrachloride–2-propanol system as shown in Figure 6. The constants of the equations are listed in Table V. The following equation represents the activity coefficient of component 1 in the ternary system.

$$\begin{aligned}\log \gamma_1 = {} & x_2(x_2 + x_3)B_{12} + x_2\{x_3(2x_1 - x_2) + x_2(3x_1 - x_2)\}C_{12} + \\ & x_2(x_1 - x_2)\{x_2(5x_1 - x_2) + x_3(3x_1 - x_2)\}D_{12} + \\ & x_3(x_2 + x_3)B_{31} - x_3\{x_2(2x_1 - x_3) + x_3(3x_1 - x_3)\}C_{31} + \\ & x_3(x_1 - x_3)\{x_3(5x_1 - x_3) + x_2(3x_1 - x_3)\}D_{31} - \\ & x_2x_3B_{23} - 2x_2x_3(x_2 - x_3)\,C_{23} - 3x_2x_3\,(x_2 - x_3)^2\,D_{23} + \\ & x_2x_3(1 - 2x_1)\,C_1 \qquad (4)\end{aligned}$$

Logarithms of activity coefficient for the other components are provided by cyclic advancement of the subscripts in the order 1,2,3,1. The value of ternary constant C_1 was determined from experimental data in the composition range of small x_1. C_2 and C_3 were determined similarly. These ternary constants differ and were retained in the equations to represent the experimental data well. Experimental data are given in Table VI. The agreement of the experimental and calculated results seems to be reasonable, if we note that the binary constants do not represent the binary equilibrium data completely, and all the binary and ternary constants were considered independent of temperature.

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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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