The System Cyclohexane–2-Propanol–Water

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The liquid-liquid equilibria at 25° C. and at the boiling temperature and the vapor-liquid equilibrium and the composition of the azeotropic mixtures at the pressure of 760 mm. of Hg of the system cyclohexane–2-propanol–water have been determined.

BOTH the liquid-liquid and vapor-liquid equilibria of the ternary system cyclohexane-2-propanol-water have been studied: the liquid-liquid equilibria at 25° C. and at the boiling temperature of the mixtures both at 760 mm. of Hg and the vapor-liquid equilibrium also under constant pressure of 760 mm. of Hg. Data have been reported in the literature on the liquid-liquid equilibrium at 25° C. and 760 mm. of Hg by Washburn and Brockway (*16*) and on the vapor-liquid equilibrium of the homogenous binary systems 2-propanol–water (*1, 2, 7, 8, 13, 18*) and cyclohexane–2-propanol (*9*), but no data on the vapor-liquid equilibrium of the ternary system have been published.

EXPERIMENTAL

Purity of Materials. The purification of materials was carried out by rectification through a glass column 3 cm. in diameter and 2 meters high, containing packings of 3 mm. in stainless steel wire, and under a reflux of at least ten. Starting from a large quantity of material and sampling many fractions, only the fractions of which the boiling point, specific gravity, and index of refraction remain constant, were kept. The physical properties of the materials used in this study are listed in Table I. Twice distilled water was used.

Analytical Method. Different sets of mixtures of known composition are prepared in this way so that the whole composition range is covered. Each set contains a constant water content and different contents of the other compounds. The sets are prepared at intervals of 10 mole % of water. The refractive index and specific gravity of these mixtures were measured to make a calculation chart by plotting the physical property against the per cent of the most volatile compound. (Figure 1). Such a chart contains a set of curves corresponding to the different water contents. From this chart, the lines for constant value of refractive index and specific gravity, included in Figure 1, are graphically derived.

The measurements of the refractive index are made by an Abbe refractometer with an accuracy of ±0.0002 and the measurements of specific gravity with an accuracy of ±0.0001. The temperature was kept constant at 25.0 ± 0.1° C. The uncertainty in observed composition was ±0.1 mole % for binary mixtures and for ternary mixtures was a function of the angle formed by the lines of constant value of refractive index and of specific gravity.

Water can be determined by the Karl Fischer titration method. The uncertainty of observed water contents was ±0.1 wt. %. For low water concentrations, it was more accurate to carry out the analysis by measurements of one physical property and titration of the water.

Heterogenous mixtures were homogenized by adding a known quantity of 2-propanol, and the analysis was carried out on this homogenous mixture.

Determination of Liquid-Liquid Equilibrium Data. The binodal curve was determined by titration of heterogenous mixtures with a homogenous mixture. The composition of the heterogenous mixture moves along the line connecting the point representing the composition of the heterogenous mixtures and the point representing the composition of the homogenous mixture. At a given point the binodal curve is reached, which makes itself manifest by transition from a turbid to a clear mixture. Since the accuracy with which the transition can be observed is sharper as the angle between the tangent to the binodal curve in the transition point and the line passing through the composition of the system during titration is nearer to a right angle, the composition of homogenous titrating mixture is chosen taking into account this consideration.

Since the quantities of titrating and titrated mixture were accurately determined by weighing, the uncertainty in the observed values was especially determined by the accuracy of observation of the transition point. This uncertainty could be taken for the whole curve to be never more than 0.05 mole %. Temperature was kept constant at 25.0 ± 0.1° C.

Table I. Physical Properties of Materials

	Boiling Point at 760 Mm. of Hg, ° C.		Specific Gravity, D_4^{25}		Refractive Index, n_D^{25}	
	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.
Cyclohexane	80.7	80.738 (*17*)	0.7738	0.77389 (*3*)	1.4238	1.42334 (*17*)
2-Propanol	80.4	80.40 (*17*)	0.7808	0.78095 (*17*)	1.3749	1.3747 (*17*)

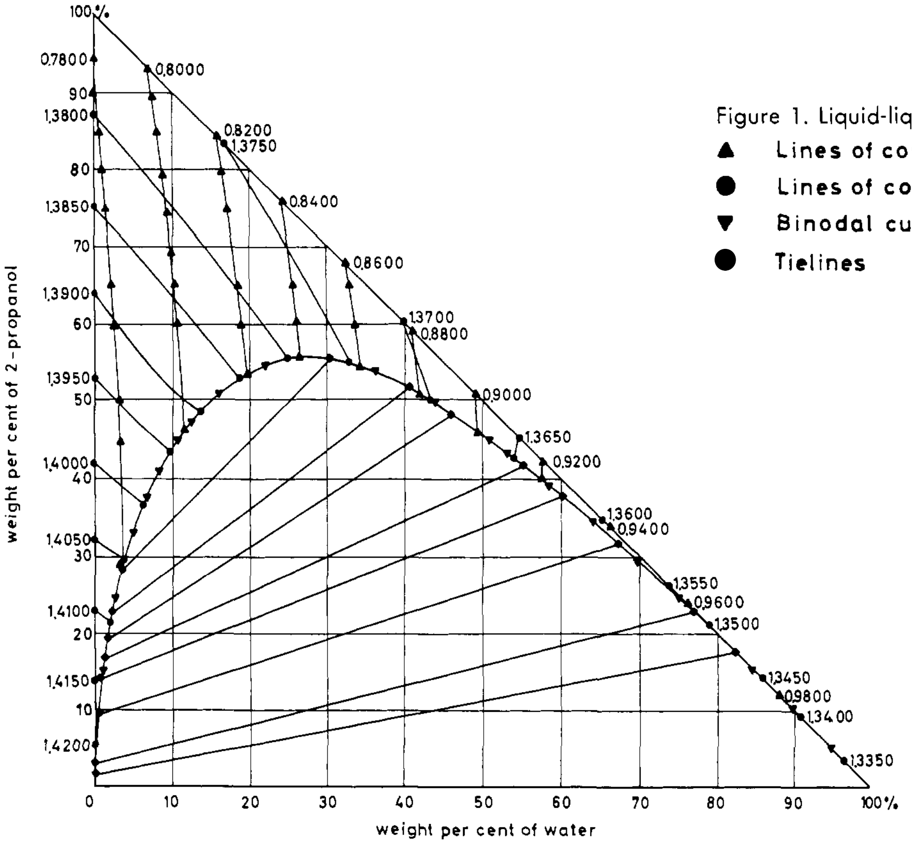

Figure 1. Liquid-liquid equilibrium at 25° C.

▲ Lines of constant value of specific gravity d_4^{25}

● Lines of constant value of refractive index n_4^{25}

▼ Binodal curve

● Tielines

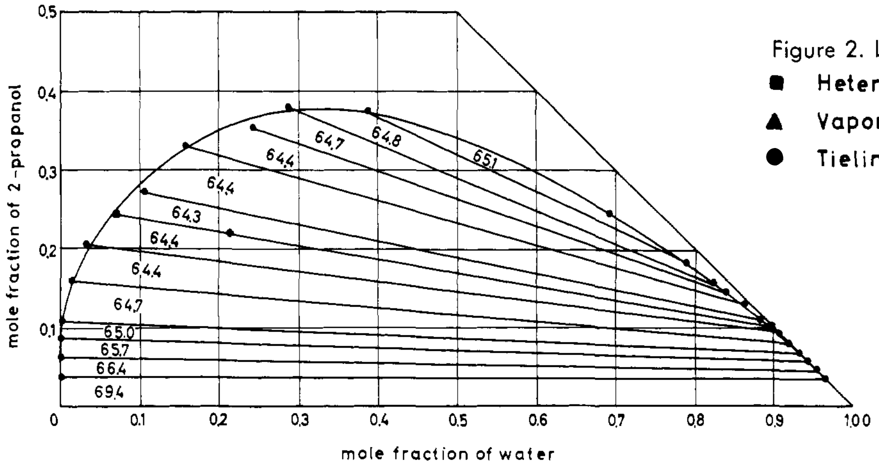

Figure 2. Liquid-liquid equilibrium at boiling point

■ Heteroazeotropic lines

▲ Vapor composition of azeotropic mixture

● Tielines

To determine the tielines, the two liquid phases were thoroughly mixed for 1 hour at constant temperature; after separation of the phases, a sample of each phase was analyzed. In this way, the two end points of a tieline were obtained.

The determination of the tielines of the liquid-liquid equilibrium at boiling temperature at 760 mm. of Hg was performed in the same way. The uncertainty in observed temperature was ±0.1° C.

Determination of Vapor-Liquid Equilibrium Data. If the condensed vapor phase formed one homogenous phase, the determination of the vapor-liquid equilibrium data was performed with an Othmer still (*10*). If this condensed vapor phase formed a heterogenous mixture, the condensate receiver of the Othmer still was replaced by a three-way stopcock. Doing this, we actually pass from a still based on the circulation principle to one based on the distillation principle. To avoid disturbance of the equilibrium when taking the vapor sample, the vessel containing the boiling liquid was substantially enlarged (to 2 liters) and the sample taken was as small as possible (20 cc.). Partial condensation in the upper part of the still was avoided by applying an external heater, which kept the temperature of the space between the tube transporting the vapor to the condenser and the external wall a little higher than the temperature of the boiling liquid. The uncertainty in observed temperature was ±0.1° C. The pressure was kept constant by means of a sulfuric acid manostat at 760.0 ± 0.5 mm. of Hg.

Determination of Composition of Azeotropic Mixtures. According to the first law of Gibbs-Konovalow the composition of an azeotropic mixture is unequivocally determined

Table II. Liquid-Liquid Equilibrium at 25° C., Wt. %

BINODAL CURVE

Cyclohexane	2-Propanol	Water
0.10	0.00	99.90
0.15	5.00	94.85
0.30	9.95	89.75
0.40	14.95	84.65
0.55	24.50	74.95
0.65	29.75	69.60
0.90	34.50	64.60
1.60	39.40	59.00
2.90	43.60	53.50
3.60	45.40	51.00
6.15	50.10	43.75
10.20	53.65	36.15
14.10	55.25	30.65
24.00	54.65	21.35
28.50	53.00	18.50
33.50	50.50	16.00
40.25	47.00	12.75
44.50	44.50	11.00
50.00	41.10	8.90
55.80	37.25	6.85
61.75	33.25	5.00
67.50	29.00	3.50
73.15	24.50	2.35
78.80	19.75	1.35
84.55	14.95	0.50
94.90	5.00	0.10
99.95	0.00	0.05

TIELINES

Cyclohexane-Rich Phase			Water-Rich Phase		
Cyclohexane	2-Propanol	Water	Cyclohexane	2-Propanol	Water
98.1	1.9	0.1	0.4	17.5	82.1
95.9	3.0	0.2	0.6	21.8	77.6
90.3	9.5	0.3	0.9	31.2	67.9
85.5	14.0	0.5	1.0	38.2	60.8
83.8	16.2	1.0	2.1	42.2	55.7
79.4	19.3	1.3	5.3	46.2	48.5
75.2	22.8	2.0	7.5	51.8	40.7
68.2	28.3	3.5	14.5	55.5	30.0

Table III. Composition of Azeotropic Mixtures

	Mole %		Boiling Point at 760 Mm. of Hg., ° C.	
	Exptl.	Lit.	Exptl.	Lit.
2-PROPANOL-WATER[a]				
2-Propanol	68.34	68.7 (*5*)	80.20	80.1 (*5*)
CYCLOHEXANE-2-PROPANOL[a]				
Cyclohexane	59.78	60.3 (*5*)	69.35	69.4 (*5*)
CYCLOHEXANE-WATER[b]				
Cyclohexane	70.10	70.0 (*5*)	69.40	69.5 (*5*)
CYCLOHEXANE-2-PROPANOL-WATER[c]				
Cyclohexane Vapor phase	56.60	54.8 (*4*)	64.30	64.3 (*4*)
2-Propanol Vapor phase	22.20	19.2 (*4*)	...	...
Cyclohexane Liquid phase	68.4	...	...	...
2-Propanol Liquid phase	24.6	...	...	...
Cyclohexane Liquid phase	0.2	...	...	...
2-Propanol Liquid phase	10.3	...	...	...

[a] Homogenous Binary Mixture (cyclohexane-rich liquid phase).
[b] Heterogenous Binary Mixture (water-rich liquid phase).
[c] Heterogenous Ternary Mixtures (water-rich liquid phase).

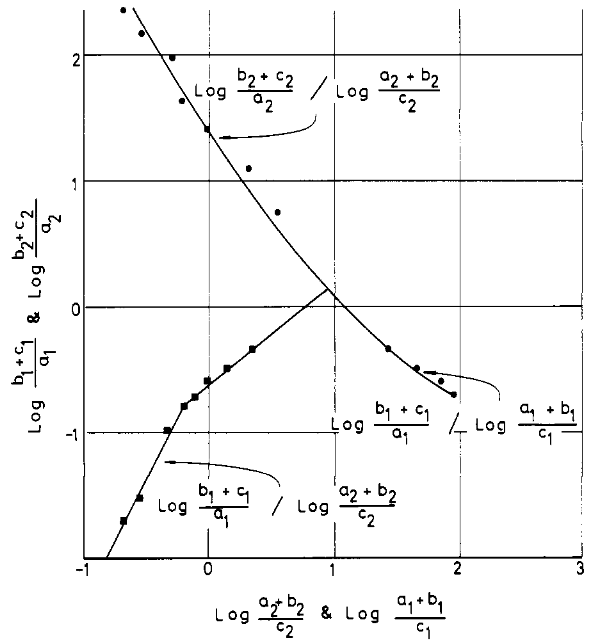

Figure 3. Correlation of the liquid-liquid equilibrium data at 25 ° C. by the method of Othmer and Tobias

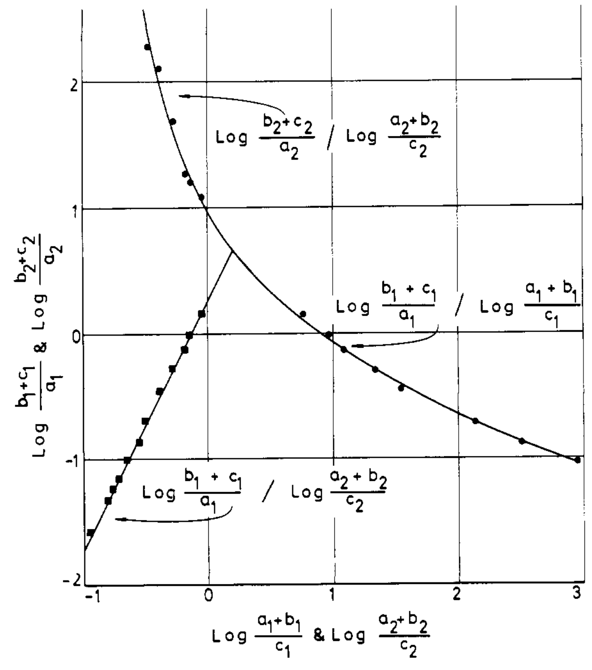

Figure 4. Correlation of the liquid-liquid equilibrium data at boiling point by the method of Othmer and Tobias

by the extremum in the boiling point isobars. The determination of the composition of the binary azeotropic mixtures is performed by means of an ebulliometric method. The entire experimental setup consists of two Swietoslawski ebulliometers (*15*) and a Wheatstone bridge in which resistances with negative temperature coefficients are built in as measuring elements. The one ebulliometer is filled with a reference liquid the other with a mixture with composition in the neighborhood of the azeotropic mixture. The bridge measures with great sensitivity (0.001° C.) changes in the temperature difference between both ebulliometers. Such

Table IV. Vapor-Liquid Equilibrium Data

	Mole Fraction in Liquid Phase			Mole Fraction in Vapor Phase			Activity Coefficients		
Temp., ° C.	Cyclohexane	2-Propanol	Water	Cyclohexane	2-Propanol	Water	Cyclohexane	2-Propanol	Water
				HOMOGENOUS LIQUID PHASE					
77.2	0.070	0.930	...	0.246	0.754	...	3.926	1.000	...
74.0	0.142	0.858	...	0.381	0.619	...	3.327	1.007	...
72.8	0.200	0.800	...	0.430	0.570	...	2.742	1.057	...
71.9	0.236	0.764	...	0.456	0.544	...	2.529	1.099	...
70.5	0.399	0.601	...	0.555	0.445	...	1.910	1.253	...
69.7	0.580	0.420	...	0.598	0.402	...	1.455	1.626	...
69.4	0.600	0.400	...	0.608	0.392	...	1.442	1.687	...
69.2	0.714	0.286	...	0.628	0.372	...	1.262	2.259	...
70.1	0.777	0.223	...	0.647	0.353	...	1.159	2.636	...
70.2	0.800	0.200	...	0.659	0.341	...	1.143	2.831	...
73.0	0.955	0.045	...	0.759	0.241	...	1.007	7.889	...
83.8	...	0.050	0.950	...	0.475	0.525	...	8.986	1.015
82.8	...	0.075	0.925	...	0.494	0.506	...	6.478	1.046
82.5	...	0.090	0.910	...	0.510	0.490	...	5.664	1.042
81.7	...	0.140	0.860	...	0.542	0.458	...	3.997	1.064
81.2	...	0.205	0.795	...	0.548	0.452	...	2.817	1.160
80.6	...	0.400	0.600	...	0.583	0.417	...	1.583	1.452
80.1	...	0.625	0.375	...	0.653	0.347	...	1.158	1.972
80.1	...	0.750	0.250	...	0.720	0.280	...	1.064	2.387
80.9	...	0.900	0.100	...	0.858	0.142	2.930	1.020	2.930
77.6	0.033	0.870	0.097	0.178	0.070	0.122	5.933	0.977	2.968
74.1	0.079	0.822	0.100	0.315	0.557	0.128	4.887	0.953	3.491
71.5	0.138	0.770	0.092	0.405	0.493	0.102	3.932	1.002	3.383
68.9	0.234	0.667	0.099	0.480	0.410	0.110	2.963	1.076	3.800
69.7	0.200	0.700	0.100	0.494	0.386	0.120	3.507	0.934	3.954
67.8	0.300	0.600	0.100	0.533	0.340	0.127	2.680	1.050	4.547
66.7	0.405	0.496	0.099	0.546	0.301	0.152	2.110	1.177	5.768
65.9	0.447	0.442	0.111	0.552	0.269	0.179	1.991	1.230	6.278
78.0	0.027	0.780	0.193	0.103	0.690	0.207	4.150	1.059	2.489
75.6	0.050	0.735	0.215	0.235	0.568	0.197	5.479	1.021	2.344
71.9	0.120	0.675	0.206	0.410	0.402	0.188	4.498	0.942	2.735
67.9	0.191	0.620	0.189	0.488	0.340	0.172	3.823	1.008	3.249
65.7	0.300	0.500	0.200	0.548	0.258	0.193	2.954	1.045	3.789
64.8	0.400	0.400	0.200	0.561	0.230	0.209	2.339	1.212	4.273
69.3	0.100	0.601	0.299	0.453	0.336	0.211	6.482	0.962	2.355
65.8	0.200	0.501	0.299	0.540	0.258	0.202	4.332	1.035	2.632
64.8	0.300	0.399	0.301	0.574	0.223	0.203	3.176	1.174	2.756
65.0	0.200	0.400	0.400	0.556	0.222	0.222	4.602	1.062	2.249
65.6	0.100	0.396	0.504	0.546	0.237	0.217	8.854	1.222	1.703
66.2	0.050	0.349	0.601	0.528	0.250	0.222	16.724	1.421	1.420
				HETEROGENOUS LIQUID PHASE					
64.7	0.300	0.300	0.400	0.566	0.222	0.212	3.141	1.570	2.178
64.4	0.300	0.200	0.500	0.565	0.223	0.212	3.177	2.399	1.766
64.4	0.350	0.150	0.500	0.566	0.215	0.218	2.723	3.083	1.816
64.5	0.400	0.100	0.500	0.584	0.204	0.213	2.449	4.375	1.766
65.7	0.450	0.050	0.500	0.589	0.169	0.232	2.109	6.855	1.820

changes occur by progressively changing the composition of the mixture. The extremum in the difference indicates the position of the azeotropic mixture. The uncertainty in the observed composition of the binary azeotropic mixtures is ±0.02 mole %.

When three compounds form a ternary heteroazeotropic mixture, then its projection onto the concentration triangle lies on the heteroazeotropic line. The end points of this line represent the composition of the two liquid phases in equilibrium with each other and with the vapor at the boiling temperature. To find the location of the heteroazeotropic line, it is necessary to examine the shape of some boiling temperature isobars in the range of intersection with this line. The examination of these isobars has been done by the same method as described above for the binary mixtures. In this case, the extremum in the difference of boiling temperature between the reference liquid and the examined liquid indicates a point on the heteroazeotropic line (*14*).

Table V. Constants of Redlich-Kister Equations for the System Cyclohexane(1)–2-Propanol(2)–Water(3)

	Binary Constants	
$B_{12} = 0.711$	$C_{12} = 0.132$	$D_{12} = 0.027$
$B_{23} = 0.657$	$C_{23} = -0.244$	$D_{23} = 0.099$
$B_{31} = 1.099$	$C_{31} = 0.000$	$D_{31} = 0.281$
	Ternary Constants	
$C_1 = 2.034$	$C_2 = 1.027$	$C_3 = 1.267$

The composition of the vapor phase of the ternary mixture was determined as the intersection of the heteroazeotropic line and the line correlating the points represented in the Gibbs composition diagram of the vapor phases in equilibrium with heterogenous liquid mixtures.

When the composition of the azeotropic mixture was known, the boiling point of this mixture was measured,

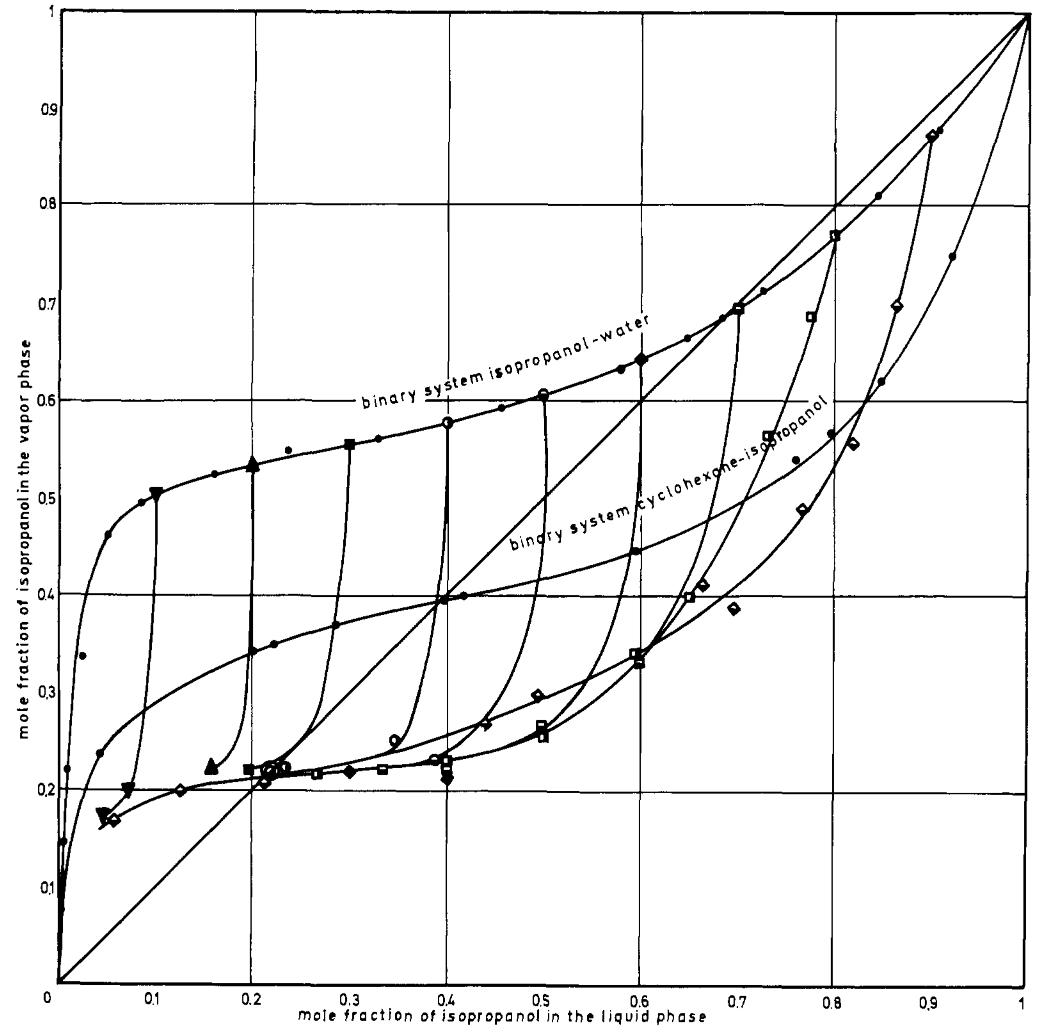

Figure 5. Ternary vapor-

⊚Azeotropic mixture

Lines of constant mole
phase

Symbol

◆
◧
⊟
●
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also in an ebulliometer of the same type. Uncertainty in observed temperature was ±0.05° C. The pressure was kept at 760.0 ± 0.5 mm. of Hg by means of a sulfuric acid manostat.

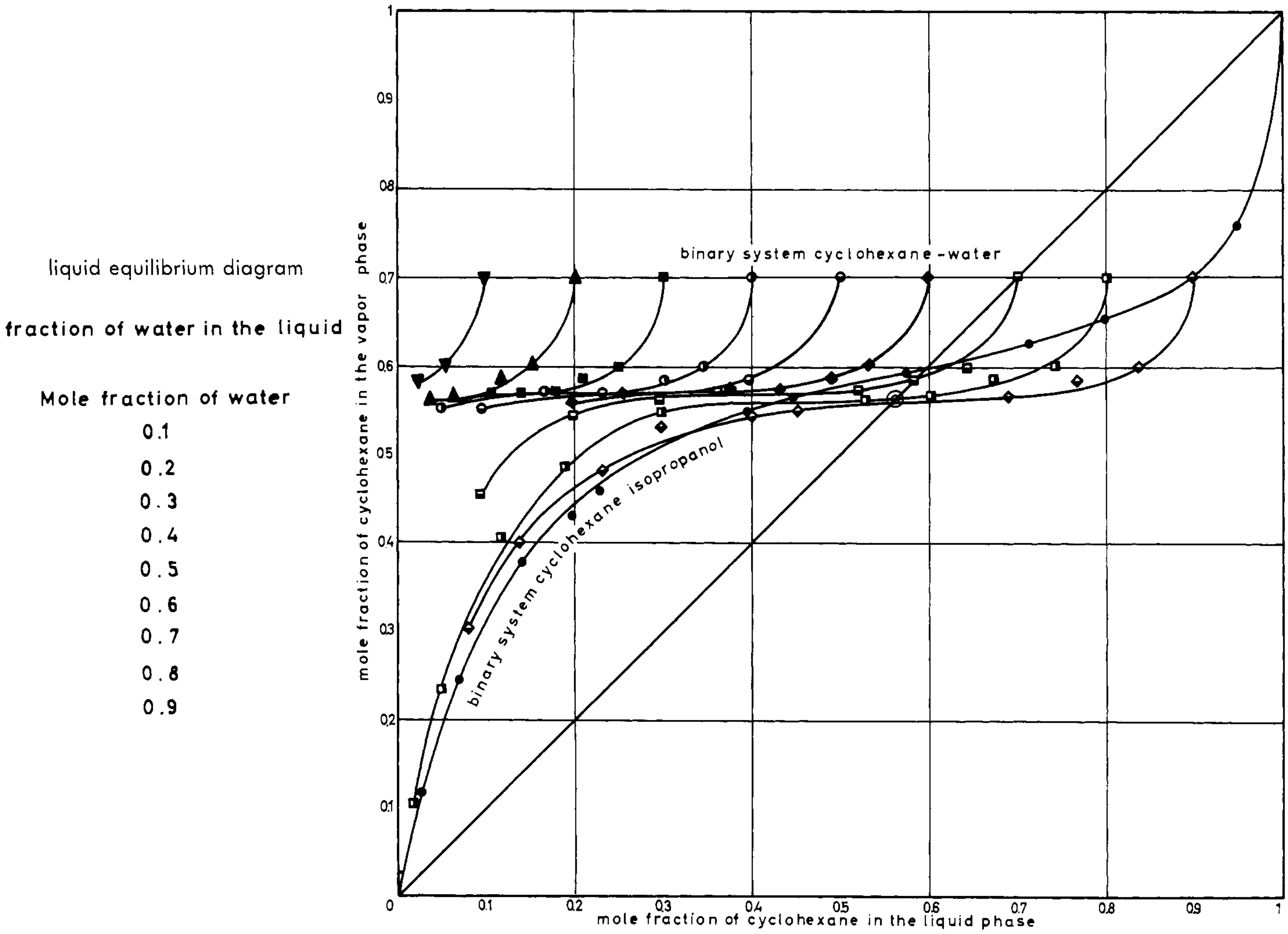
RESULTS AND THERMODYNAMIC ANALYSIS

Figure 1 represents the liquid-liquid equilibrium diagram at 25° C. and 760 mm. of Hg, containing the binodal, tielines, and also lines of constant value of specific gravity (d_4^{25}) and refractive index (n_D^{25}). The data about the binodal and tielines are also listed in Table II.

Figure 2 represents the liquid-liquid equilibrium diagram at boiling temperature and 760 mm. of Hg. It also contains the heteroazeotropic line, which also forms a tieline in this diagram. This diagram is of importance for the determination of the vapor-liquid equilibrium of the heterogenous mixtures since it permits the determination of this equilibrium for the complete heterogenous part of the diagram with a relatively small number of experiments. Each heterogenous mixture, of which the composition is represented by a point of the same tieline whatever the ratio of both phases is, is in equilibrium with a vapor phase of the same composition. Consequently, it is sufficient to determine the vapor-liquid equilibrium for a heterogenous mixture with an arbitrary ratio of both phases to know the vapor-liquid equilibrium for all mixtures of which the composition is represented by a point of the same tieline. The composition of the conjugated phases can be correlated by the equation of Othmer and Tobias (*11*) as Figures 3 and 4 show.

The composition of the binary and ternary azeotropic mixtures is listed in Table III. The vapor-liquid equilibrium data are listed in Table IV and represented in Figure 5.

Experimental activity coefficients for the components are calculated neglecting vapor phase imperfection. The vapor pressure of pure components are taken from literature (*6*, *12*). Values of activity coefficients smaller than one are due to random errors. The experimental values of binary systems are correlated with the three-constant Redlich-Kister equations. These of the ternary system are correlated with the Redlich-Kister equation containing the binary constants and one ternary constant. The ternary constants corresponding with the different components differ and have to be retained to represent the experimental data well. The constants are listed in Table V. The agreement of the experimental and calculated values seems to be quite good for binary systems and reasonable for ternary systems taking into account that all constants have been considered to be independent of temperature. The root mean square deviation between the calculated logarithms of the activity coefficients and the logarithms of the experimental values of this coefficient is, in the case of the homogenous binary system cyclohexane–2-propanol, for the cyclohexane 2.10^{-2} and for the 2-propanol 1.10^{-2}. This value is, for the homogenous binary system 2-propanol–water, for 2-propanol 5.10^{-2} and for water 1.10^{-2}. Also, the logarithm of the activity coefficients of the heterogenous mixture cyclohexane-water is correlated with the Redlich-Kister equation to obtain the third set of binary constants. The root mean square deviation calculated for nine equidistant



values of composition, is in this case for both components 3.10^{-2}.

For the ternary system, this value is for cyclohexane 8.10^{-2}, for 2-propanol 6.10^{-2}, and for water 4.10^{-2}.

Comparison with Previous Work. There is little agreement between the published data for the vapor-liquid equilibria of the binary system 2-propanol–water, except for the data published by Brunjes and Bogart (*1*) and by Wilson and Simons (*18*) in the concentration range above 0.3 mole fraction. The present data agree with the data of Brunjes and Bogart in the whole concentration range. The only previous work reported on the system 2-propanol–cyclohexane is that of Nagata (*9*). The present work agrees with these data.

On the liquid-liquid equilibrium at 25° C. of the ternary system, data have been published by Washburn and Brockway (*16*). The present data agree with these data concerning the position of the binodal curve, but there is a little difference in the position of the tielines.

For comparison of the present data on the composition of azeotropic mixtures, some data from the literature (*4*, *5*) are also listed in Table III.

ACKNOWLEDGMENT

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