Vapor-liquid–equilibrium Data for the Ternary System Cyclohexane-heptane-toluene

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Previous papers have reported equilibrium data for the binary systems cyclohexane-heptane, heptane-toluene, and cyclohexane-toluene. This present study gives similar data for the ternary system cyclohexane-heptane-toluene and compares the activity coefficients with those predicted from the three limiting binaries.

The ternary activity coefficients fall well in line between the limiting-binary data. Distribution is about as would be predicted by the ternary Margules equations. As an approximation, if the coefficients are plotted as a function of the aromatic concentration only, without consideration of the ratio of naphthenes to paraffins, reasonably good correlation is observed.

Previous papers (*1, 3, 4*) have reported equilibrium data for the binary systems cyclohexane-heptane, heptane-toluene, and cyclohexane-toluene. This work gives ternary equilibrium-data for the system cyclohexane-heptane-toluene and compares the computed activity coefficients with those predicted from the three limiting-binaries.

APPARATUS

The equilibrium apparatus, Figure 1, has been described in detail in an earlier article (*1*). It is of the vapor-recirculating type and uses a vapor jacket to maintain adiabatic operation. All parts are glass except for the Teflon sample valves. The heating elements, which are fused into a borosilicate glass tube, are completely enclosed with glass. Except for sampling, operation is entirely automatic.

PURIFICATION OF HYDROCARBONS

All three of the hydrocarbons used in this work were purified before use. Complete details concerning the source, the method of purification, and the physical properties are given in earlier articles (*2, 3*).

ANALYSIS

Normally, the chief problem involved in studying a ternary system is that of analysis. The system cyclohexane-heptane-toluene is ideal for a naphthene-paraffin-aromatic study, because it can be analyzed simply and accurately. As

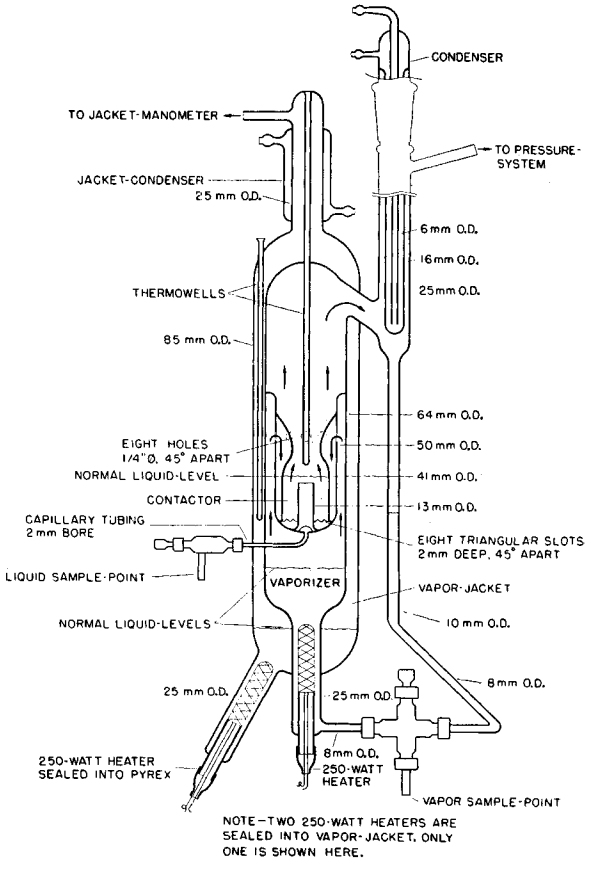

Fig. 1. Vapor-recirculating still.

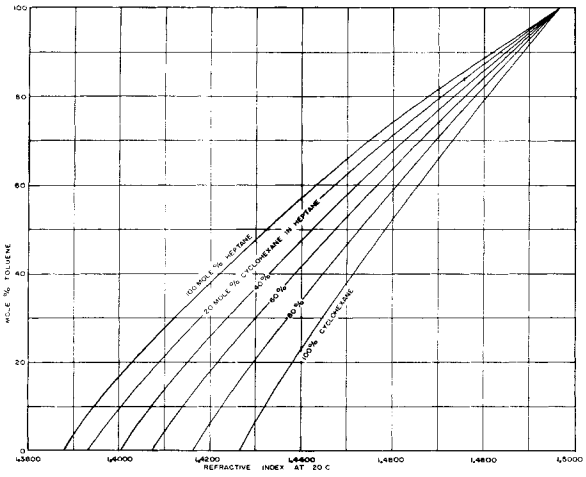

Fig. 2. Toluene analysis, cyclohexane-heptane-toluene mixtures.

toluene can be removed quantitatively from cyclohexane and heptane with concentrated sulfuric acid at room temperature without affecting either the cyclohexane or the heptane, it is possible to analyze mixtures of these three hydrocarbons by reading the refractive index before and after acid extraction. Calibration curves, shown in Figure 2, were made up with known mixtures. In addition to these curves, one requires the refractive-index–composition curve for the cyclohexane-heptane binary, which was determined previously (*4*).

Extractions were made in cream-test bottles with an acid-to-hydrocarbon ratio of 10 to 1. Fifteen minutes in the laboratory shaker was found to be sufficient time for complete toluene extraction.

Tests made with known mixtures showed that the acid-extraction step in the analytical procedure does not appreciably decrease the precision. Accuracy is limited primarily by the reproducibility in refractometer readings. The worst case is represented by the cyclohexane-heptane binary, where there is a spread of 385 fourth-place points on the refractometer between the pure components. Refractometer readings can be reproduced to ±1 point, an accuracy of about ±0.25%.

RANGE

All three of the limiting-binary mixtures for this ternary system had been studied earlier (*1, 3, 4*). In order to cover the entire range of intermediate ternary compositions, mixtures containing 20 mole % cyclohexane in heptane, 40 mole %, 60%, and 80% were blended. Each of these mixtures was then studied in the still with varying amounts of toluene.

All work was carried out isobarically at 760 mm. Hg absolute pressure.

RESULTS

Experimental equilibrium data for the ternary system, along with computed activity coefficients, are listed in Tables 1, 2, 3, and 4. Similar data for the three limiting binaries were reported earlier (*1, 3, 4*).

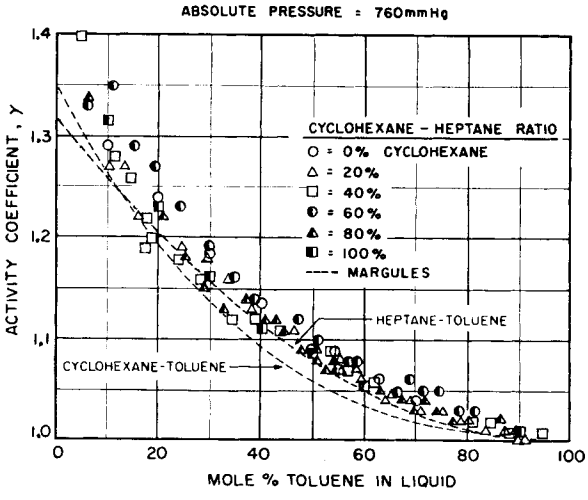

Fig. 3. Toluene activity coefficients, system—cyclohexane, heptane, toluene. Absolute pressure = 760 mm. Hg.

Toluene

Figure 3 is a plot of the activity coefficients for toluene computed from the experimental data.

The binary coefficients for toluene in cyclohexane and in heptane are also

Table 1

Vapor-liquid-equilibrium Data, Cyclohexane-Heptane-Toluene Ratio—Cyclohexane to Heptane = 0.25 in Charge to Still Absolute Pressure = 760 mm. Hg

Temp.,	Composition, mole % Liquid		Vapor		Activity coefficient		
°C.	CH	C7	CH	C7	CH	C7	Tol
95.0	15.7	81.8	23.3	74.8	0.99	1.01	1.20
95.6	14.4	75.2	21.7	69.8	0.99	1.01	1.27
96.1	14.0	69.5	21.2	65.8	0.98	1.01	1.22
96.75	12.3	62.8	19.0	61.3	0.98	1.02	1.19
97.2	11.3	58.8	17.8	57.5	0.99	1.01	1.18
97.65	10.6	55.5	17.1	56.0	1.00	1.03	1.16
98.15	9.7	52.0	16.1	53.8	1.01	1.04	1.13
98.75	9.2	47.8	15.7	50.3	1.02	1.04	1.12
99.1	8.7	45.3	14.6	48.9	1.00	1.06	1.11
99.7	7.9	41.2	14.0	44.7	1.03	1.07	1.09
100.25	7.3	37.6	12.9	43.1	1.02	1.08	1.08
100.25	7.5	36.6	13.4	32.5	1.02	1.10	1.07
100.8	6.7	34.6	11.9	40.9	1.02	1.10	1.07
100.9	7.2	33.2	12.7	39.8	1.00	1.12	1.06
101.35	6.1	31.4	11.3	38.3	1.04	1.12	1.06
101.5	6.0	30.0	11.4	37.5	1.05	1.14	1.04
101.9	5.4	29.1	10.4	36.4	1.06	1.13	1.05
102.4	5.3	26.0	10.3	33.7	1.06	1.15	1.04
102.8	4.9	24.1	9.7	31.8	1.07	1.16	1.03
103.6	4.2	20.1	8.6	27.7	1.07	1.19	1.03
104.8	3.3	16.5	6.9	24.3	1.07	1.23	1.02
105.7	2.7	13.4	5.7	20.0	1.06	1.21	1.01
106.5	2.2	10.5	4.8	16.9	1.07	1.28	1.01
107.0	1.9	8.7	4.2	14.8	1.11	1.32	1.00
107.6	1.4	7.1	3.5	12.4	1.18	1.35	1.00

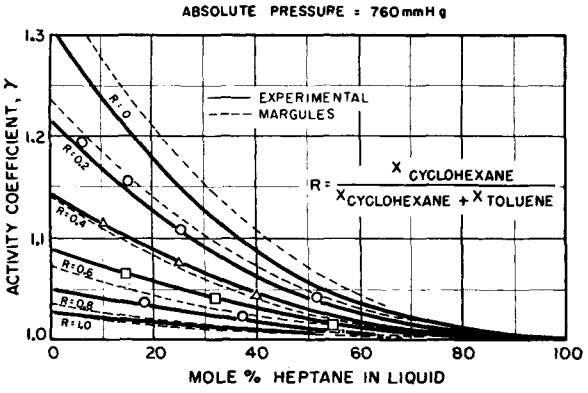

Fig. 4. Heptane activity coefficients, system—cyclohexane, heptane, toluene. Absolute pressure = 760 mm. Hg.

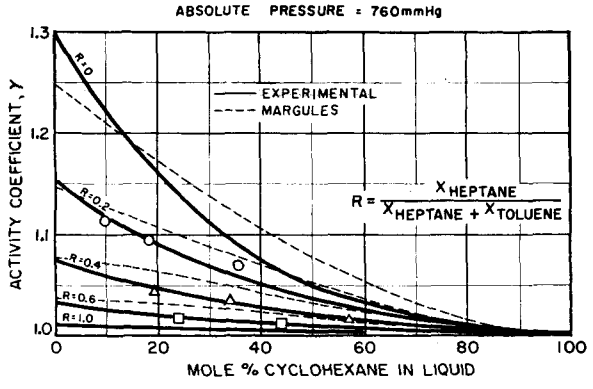

Fig. 5. Cyclohexane activity coefficients, system—cyclohexane, heptane, toluene. Absolute pressure = 760 mm. Hg.

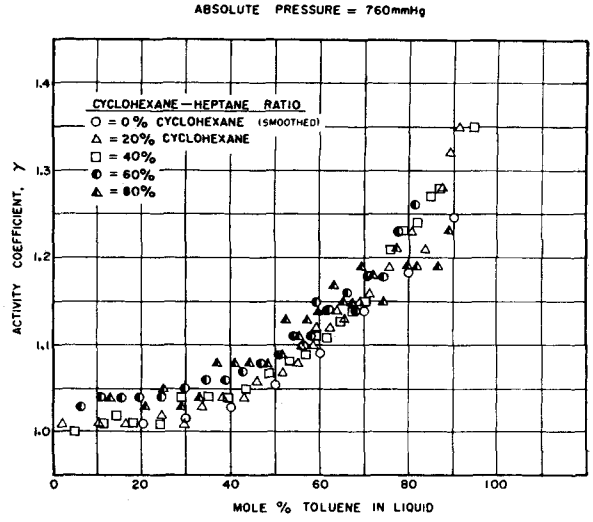

Fig. 6. Heptane activity coefficients, system—cyclohexane, heptane, toluene. Absolute pressure = 760 mm. Hg.

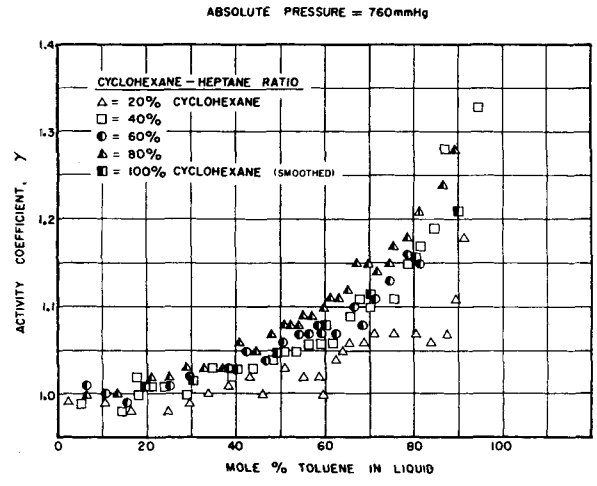

Fig. 7. Cyclohexane activity coefficients, system—cyclohexane, heptane, toluene. Absolute pressure = 760 mm. Hg.

plotted. It can be seen from this plot that the activity-coefficient curve for toluene is essentially the same in cyclohexane as in heptane and in all ternary mixtures with cyclohexane and heptane that were studied.

The activity coefficients discussed here are defined as $\pi Y/PX$ where π is the total pressure of the system and P is the vapor pressure of the pure component at the system temperature. Vapor pressures were taken from data published by the National Bureau of Standards, A.P.I. Project 44 (1953).

Heptane

The binary activity-coefficient curve for heptane in toluene is quite different from the curve for heptane in cyclohexane, as can be seen in Figure 4. As would be expected, the ternary activity coefficients for heptane fall between the curves for the two limiting binaries. The lines shown in Figure 4 as representing the binary activity coefficients are smoothed curves. The data points have been omitted for

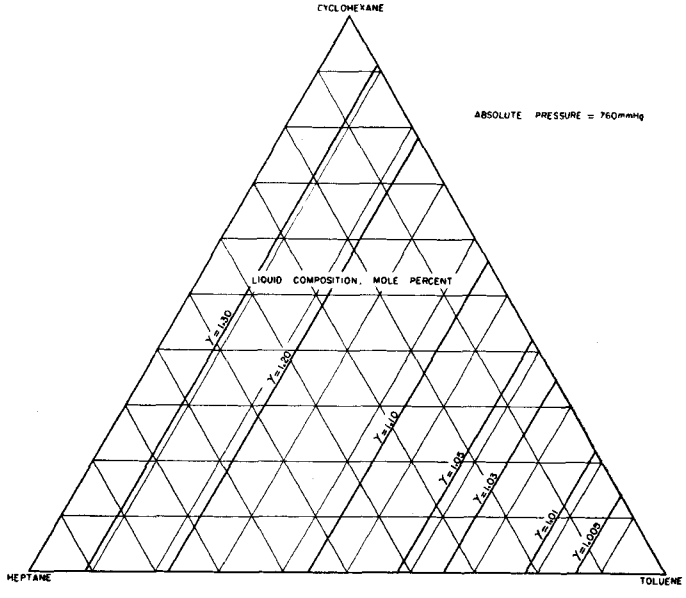

Fig. 8. Toluene activity coefficients—cyclohexane, heptane, toluene. Absolute pressure = 760 mm. Hg.

sake of clarity but are shown later in Figure 11. The ternary points shown in Figure 4 represent experimental values but cannot be plotted directly from the tabulated data. First the heptane activity coefficients from Tables 1 to 4 are plotted against percentage of heptane, with the *various cyclohexane*-heptane ratios as parameters. Then, with the same parameters, the activity coefficients are plotted against the ratio of heptane to heptane

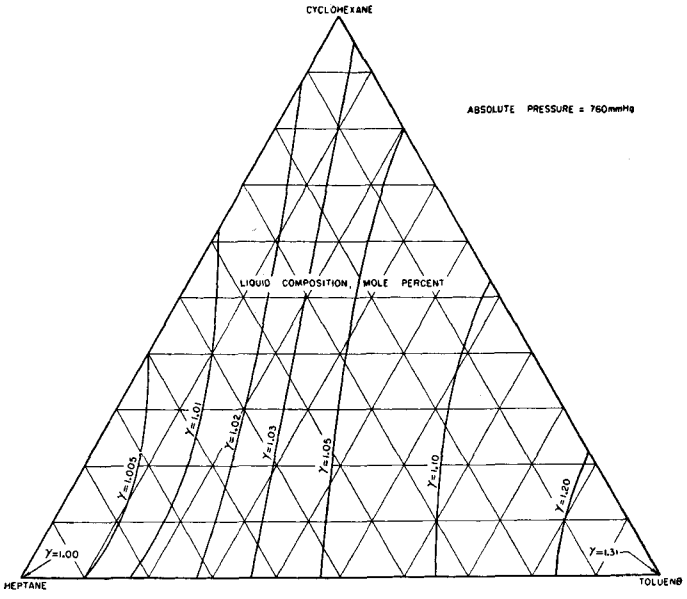

Fig. 9. Heptane activity coefficients, cyclohexane, heptane, toluene. Absolute pressure = 760 mm. Hg.

plus toluene. From these two plots, Figure 4 can be constructed.

Cyclohexane

Figure 5 shows the corresponding activity-coefficient curves for cyclohexane. As is the case for heptane, the ternary points fall in line between the limiting-binary curves.

Approximate Correlation

Another way of plotting the activity coefficients for cyclohexane and heptane is to plot them as a function of the toluene concentration only; that is, the effect

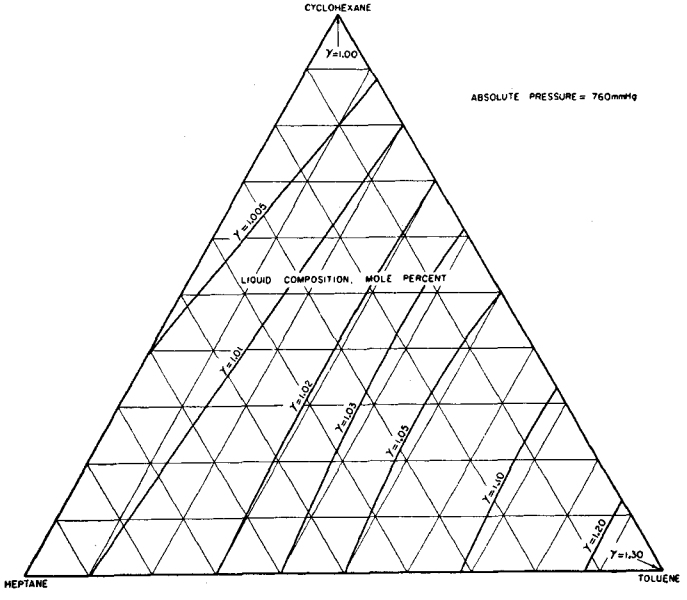

Fig. 10. Cyclohexane activity coefficients, cyclohexane, heptane, toluene. Absolute pressure = 760 mm. Hg.

of the varying naphthene-paraffin ratio is neglected. Figure 6 shows such a plot for heptane. There is some scatter in the points but they fall in a fairly narrow band.

For cyclohexane, in Figure 7, the scatter is worse, but there is still a rough correlation.

The value of such an approximate correlation does not, of course, lie in predicting ternary data. There are better procedures for ternaries. But when the designer is faced with a multicomponent problem on a mixture containing all three molecular types, he either must assume that the mixture is ideal, or he must

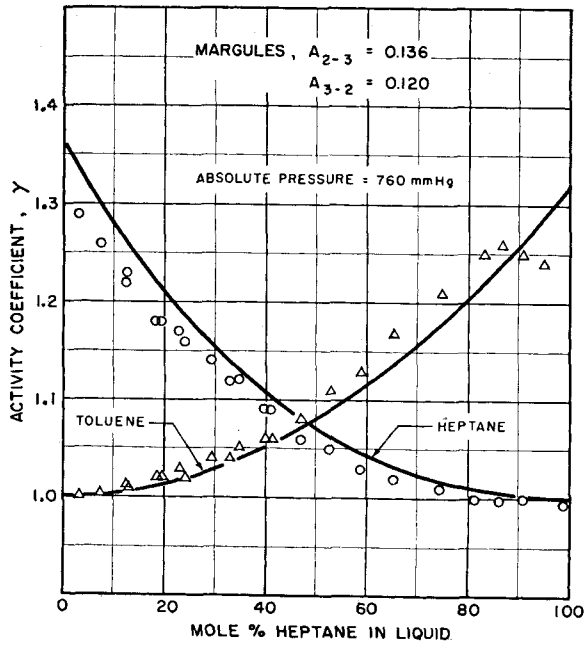

Fig. 11. Activity coefficients, heptane-toluene.

assign some arbitrary values for the activity coefficients. Here is a reasonable basis for choosing these values.

Alternative Plot

An alternative method of plotting ternary activity coefficients is shown in Figures 8, 9, and 10, in which lines of constant activity coefficient are plotted on a triangular diagram. There are advan-

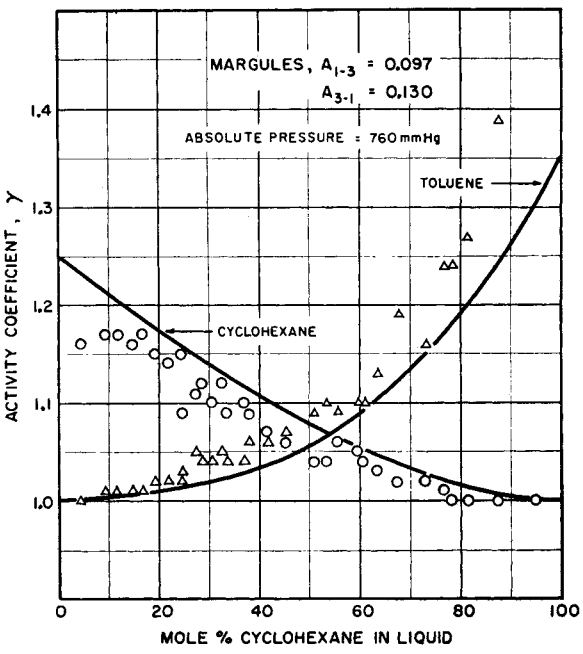

Fig. 12. Activity coefficients, cyclohexane-toluene.

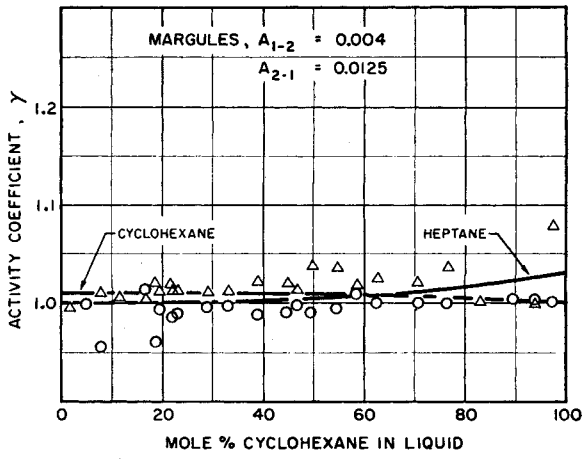

Fig. 13. Activity coefficients, cyclohexane-heptane.

tages for both types of plots. The first type, Figures 3, 4, and 5, is usually better for working up experimental data. Interpolation is normally more obvious than with a triangular plot. If only the limiting-binary data are known, the intermediate activity-coefficient lines can be sketched in by eye between the binary curves as a rough approximation.

For actually using the activity-coefficient curves, however, as in making tray calculations, the triangular plots are more convenient. Activity coefficients can be read directly as a function of the ternary composition, not as a ratio of compositions.

Ternary Curves from Binary Data

Complete vapor-liquid-equilibrium data for ternary systems are rare in the literature, and quaternary data are practically nonexistent. When designers need such information, they frequently attempt to predict the ternary or quaternary system from binary data by means of one of the thermodynamic equations. The ternary and quaternary Margules equations derived by Wohl and described by Perry (*5*) are most commonly used. These equations are derived from the two-constant, binary Margules equations and make the same simplifying assumptions plus one or two more. Nowhere in the literature have they been checked with experimental data. The present data, on a hand-picked system of a naphthene, a paraffin, and an aromatic seemed to offer a good opportunity of checking the theoretical equations.

The first step in predicting ternary activity coefficients from binary data by the Margules equations is to evaluate the Margules constants for each of the three limiting binaries. Figures 11, 12, and 13 show how this was done for heptane-toluene, cyclohexane-toluene, and cyclohexane-heptane. For each system the lines represent what were considered the best pair of Margules curves through the data points. This, of course, is somewhat a matter of personal interpretation, but in general the philosophy is to get the best average fit over the widest possible area without too much reliance on data points near the pure materials, where the accuracy is poorest. The constants for each binary are listed on the plots and are numerically equal to the logarithms of the terminal activity coefficients indicated by the Margules curves.

The dotted lines on Figures 3, 4, and 5 show the ternary activity coefficients

Table 2

Vapor-liquid-equilibrium Data, Cyclohexane-heptane-toluene Ratio—Cyclohexane to Heptane = 0.67 in Charge to Still Absolute Pressure = 760 mm. Hg

Temp.,	Composition, mole % Liquid		Vapor		Activity coefficient		
°C.	CH	C7	CH	C7	CH	C7	Tol
91.2	36.1	58.9	48.4	47.7	0.99	1.00	1.40
91.8	33.8	55.0	46.3	45.7	0.99	1.01	1.28
92.65	31.2	50.8	43.9	43.3	1.00	1.01	1.22
92.8	30.5	51.0	43.5	43.5	1.01	1.01	1.20
92.45	30.4	51.8	43.75	44.05	1.02	1.01	1.19
92.3	32.6	53.0	44.6	45.0	0.98	1.02	1.26
93.4	28.2	47.8	41.2	42.0	1.01	1.01	1.18
94.05	27.0	44.0	39.4	40.2	1.00	1.04	1.16
94.65	24.5	40.9	37.5	38.6	1.03	1.05	1.12
95.45	22.7	38.1	35.4	36.6	1.02	1.04	1.12
96.15	21.0	35.2	33.7	34.8	1.03	1.05	1.11
96.85	19.3	32.2	31.9	32.8	1.04	1.07	1.09
97.2	18.1	31.3	30.4	32.3	1.05	1.07	1.09
97.7	16.9	29.3	28.9	31.0	1.05	1.08	1.09
98.3	15.9	27.4	27.8	29.8	1.06	1.09	1.07
98.85	14.8	25.7	26.3	28.8	1.06	1.11	1.07
99.4	13.9	24.2	25.1	27.6	1.06	1.11	1.06
100.0	12.6	22.2	23.6	26.3	1.09	1.13	1.05
100.5	11.6	20.6	22.5	25.0	1.11	1.14	1.04
101.1	10.8	19.2	21.2	23.8	1.10	1.15	1.03
102.1	8.8	15.9	17.8	21.4	1.11	1.21	1.03
102.8	7.6	13.7	16.2	19.3	1.15	1.23	1.02
103.7	6.5	11.8	14.3	17.2	1.17	1.24	1.02
104.55	5.4	9.9	12.5	15.0	1.19	1.27	1.02
105.35	4.2	8.6	10.8	13.3	1.28	1.28	1.01
107.7	1.8	3.9	5.1	6.8	1.33	1.35	1.01

TABLE 3

VAPOR-LIQUID–EQUILIBRIUM DATA, CYCLOHEXANE-HEPTANE-TOLUENE RATIO—CYCLOHEXANE TO HEPTANE = 1.5 IN CHARGE TO STILL ABSOLUTE PRESSURE = 760 MM. HG

Temp.,	Composition, mole % Liquid		Vapor		Activity coefficient		
°C.	CH	C7	CH	C7	CH	C7	Tol
88.0	51.7	42.1	64.5	31.3	1.01	1.03	1.33
88.7	49.0	40.0	61.3	31.0	1.00	1.04	1.35
89.3	46.6	37.9	59.5	30.0	0.99	1.04	1.29
89.95	44.2	36.1	57.6	29.0	1.00	1.04	1.27
90.65	41.3	34.3	55.5	28.2	1.01	1.04	1.23
91.45	38.2	32.0	52.9	27.3	1.02	1.05	1.19
92.15	35.4	30.1	50.7	26.5	1.03	1.06	1.16
92.9	32.9	28.3	48.6	25.5	1.03	1.06	1.14
93.6	30.7	26.4	46.6	24.6	1.05	1.07	1.12
94.35	28.5	24.4	44.0	23.4	1.04	1.08	1.12
95.15	26.4	22.7	42.4	22.4	1.06	1.09	1.10
95.8	24.6	21.3	40.4	21.8	1.07	1.11	1.09
96.3	23.1	20.1	38.5	21.3	1.07	1.10	1.08
96.7	22.0	19.6	37.5	20.7	1.08	1.11	1.08
97.0	21.6	18.8	36.8	20.4	1.07	1.15	1.07
97.8	19.9	18.5	34.8	19.6	1.07	1.14	1.06
98.45	17.9	15.8	32.8	18.4	1.10	1.16	1.05
99.1	16.7	14.7	30.4	17.1	1.08	1.14	1.06
99.8	15.1	13.3	28.8	16.4	1.11	1.18	1.05
100.55	13.5	12.0	26.7	15.1	1.13	1.18	1.05
101.6	11.3	10.2	23.8	13.7	1.16	1.23	1.03
102.7	9.7	8.8	20.9	12.4	1.15	1.26	1.03

TABLE 4

VAPOR-LIQUID–EQUILIBRIUM DATA, CYCLOHEXANE-HEPTANE-TOLUENE RATIO—CYCLOHEXANE TO HEPTANE = 4.0 IN CHARGE TO STILL ABSOLUTE PRESSURE = 760 MM. HG

Temp.,	Composition, mole % Liquid		Vapor		Activity coefficient		
°C.	CH	C7	CH	C7	CH	C7	Tol
84.55	72.7	21.0	81.4	14.8	1.00	1.08	1.34
85.7	67.3	19.3	78.3	13.7	1.00	1.04	1.27
86.9	61.1	17.9	74.5	13.0	1.02	1.03	1.22
87.6	57.9	17.0	72.6	12.9	1.02	1.05	1.18
88.4	54.7	16.2	70.6	12.3	1.03	1.03	1.15
89.1	51.9	15.1	68.5	11.9	1.03	1.04	1.13
90.0	48.4	14.3	65.3	12.0	1.03	1.08	1.14
90.7	45.6	13.5	63.4	11.6	1.06	1.08	1.12
91.45	42.7	12.9	61.1	11.3	1.05	1.08	1.11
92.2	39.6	12.4	58.9	11.1	1.07	1.08	1.09
92.9	37.3	11.6	57.0	10.8	1.08	1.09	1.08
93.1	36.0	11.4	55.8	11.0	1.08	1.13	1.07
93.5	35.0	11.0	54.6	10.6	1.08	1.11	1.08
93.85	33.7	10.8	53.6	10.5	1.09	1.11	1.07
94.25	32.7	10.3	52.5	10.3	1.09	1.13	1.07
94.9	30.7	9.5	50.5	9.8	1.10	1.14	1.06
95.3	29.3	9.1	49.4	9.5	1.11	1.14	1.06
95.8	28.2	8.6	48.3	9.3	1.11	1.17	1.05
96.4	26.4	8.3	46.3	9.0	1.12	1.15	1.05
96.85	24.5	7.8	44.6	8.6	1.15	1.15	1.04
97.5	23.0	7.1	42.8	8.2	1.15	1.19	1.03
98.3	21.4	6.7	40.2	7.9	1.14	1.18	1.04
99.1	19.5	6.3	38.0	7.4	1.15	1.15	1.03
100.0	17.3	5.5	35.1	6.9	1.17	1.21	1.02
100.7	15.9	5.2	32.9	6.6	1.18	1.19	1.02
101.6	13.7	4.6	29.8	6.0	1.21	1.19	1.02
103.65	9.8	3.4	23.1	4.7	1.24	1.10	1.02
104.7	7.9	2.8	19.7	4.1	1.28	1.23	1.01

that are predicted when the six binary constants from Figures 11, 12, and 13 are used in the ternary Margules equation. The constant C in the ternary equation was computed from the relation

$$C = \tfrac{1}{2}(A_{2-1} - A_{1-2} + A_{1-3} - A_{3-1} + A_{3-2} - A_{2-3})$$

where the A's are the six binary constants.

Agreement between the predicted and the experimental curves for the ternary system is about as good as the agreement between the Margules curves and the experimental curves for the three binaries. The chief cause of disagreement is believed to be the effect of changing temperature on the activity coefficients. Earlier work (*4*) has shown that the various thermodynamic consistency equations sometimes do not fit isobaric data, even though similar isothermal data, determined in the same equipment, are fitted closely.

CONCLUSIONS

Vapor-liquid–equilibrium data for the ternary system cyclohexane-heptane-toluene fall in line among the data for the three limiting binaries. The ternary Margules equation is able to predict the ternary activity-coefficients from the binary data with about the same precision as the binary Margules fits the binary data, but the agreement is not very good. This lack of agreement is believed due to the effect of changing temperature on the activity coefficients. Unfortunately, the addition of a temperature-correction term to the Margules equations, even if the proper correction term were known, makes the equations extremely difficult to use for ternary or multicomponent mixtures. The uncorrected equations are probably satisfactory for isothermal data or for isobaric data where the temperature spread is small, but they should be used with caution over wide temperature ranges.

For the cyclohexane-heptane-toluene system, if the activity coefficients are plotted only as a function of the aromatic concentration, without consideration of the ratio of naphthenes to paraffins, an approximate correlation is observed. This is probably true for all ternary mixtures of naphthenes, paraffins, and aromatics.

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