Vapor-Liquid Equilibrium Data for Multicomponent Mixtures Containing Hydrocarbon and Nonhydrocarbon Components

LYMAN YARBOROUGH
Amoco Production, Tulsa, Okla. 74102

Experimental vapor-liquid equilibrium phase composition data and K values are presented for 43 multicomponent mixtures containing nitrogen, methane, carbon dioxide, ethane, hydrogen sulfide, propane, n-pentane, n-heptane, toluene, and n-decane. Data were measured at temperatures from —50–250°F and for pressures from 100–4500 psia. An unusual physical attraction was observed to exist between hydrogen sulfide and toluene, and the magnitude of the attraction depended on temperature. Published K values for n-heptane and toluene, measured in binary systems with methane, were in error at temperatures below 0°F and pressures less than 1000 psia.

Vapor-liquid equilibrium K values are used for calculations where liquid and vapor phases coexist. K values for hydrocarbons can be used to describe the phase behavior of petroleum reservoir fluids during primary depletion calculations and in secondary recovery operations such as gas cycling, miscible flooding, and thermal methods. The performance of gas-liquid surface separation equipment and separation processes in natural gas plants and refineries are predicted by using K values. In many instances, K values, which would correctly predict equilibrium phase behavior for the above processes, cannot be calculated from existing correlations, and estimates which are not so reliable as desired or experimental test results must be used.

The ultimate answer to this problem is the development of an accurate general correlation for predicting K values. Unfortunately no such correlation exists at the present time. K-value correlations are generally developed using binary data, and the final results are usually tested using data for those same binary systems or for ternary systems. The need for good multicomponent mixture data to use for testing and evaluating K-value correlations is evident. No systematic study of the effects of pressure, temperature, hydrocarbon molecular type, and the major naturally occurring nonhydrocarbons (nitrogen, carbon dioxide, and hydrogen sulfide) on K values has been reported.

To provide data for testing and evaluation of K-value calculation methods, experimental K values for synthetic multicomponent mixtures were measured over a wide range of temperature and pressure. Synthetic mixtures were employed to limit the number of components in the mixture and provide significant concentrations of each component. Also the physical properties of each component used in the mixture were well known which should allow a satisfactory test of K-value correlations. The pure components comprising the mixtures employed in this study were selected because of the large amount of K-value data available for the binary pairs.

EXPERIMENTAL

The equilibrium cell, sampling valves, and the experimental procedures used in this work have been described (17). Two different chromatographs were used for analysis during this study. Because of the wide range of volatilities of the components two chromatographic columns were used in both chromatographs to obtain a fast analysis. The columns in the first chromatograph used were 30 wt % Apiezon "L" on 60-80 mesh Chromosorb "P" packed in 9 ft of 0.25-in. tubing and 30 wt % DC Silicone 200/500 on 60-80 mesh Chromosorb

"P" packed in 30 ft of 0.25-in. tubing connected by flow switching valves. The light components (through n-pentane) were allowed to pass through the Apiezon column (held at 325°F) and were trapped in the silicone column (held at 167°F) by using two switching valves. Nitrogen and carbon dioxide impurities were not separated from methane by this silicone column. The components heavier than n-pentane were separated in the Apiezon column and were sent to a Gow-Mac thermal conductivity detector. After the heaviest component had eluted, the silicone column was switched back into the flow stream and the light components eluted to the detector. The time for complete analysis was 24 min. The component areas were digitized using a calibrated Perkin-Elmer printing integrator. The method of relative response was used to determine the composition of the sample. All switching valves and flow lines were enclosed in a constant temperature air bath held at 350°F.

The second chromatograph and the calibration procedure used in this work have been described (17). This chromatograph had a hydrogen flame ionization detector required to measure accurately the small concentration of heavy components in the vapor phase at temperatures below 150°F.

The precision of the sample analyses is difficult to judge. The principal problem is obtaining a representative sample from an equilibrium, two-phase system. The precision of the chromatograph can be separated from the precision of the sample analyses for the equilibrium phases by studying the analyses of the single-phase samples used for calibration. The precisions of the chromatographs used are estimated in Table I.

Table I. Estimated Precision of Chromatographs Used in Study

Mole fraction of component	Estimated error, % of mole fraction	
	First chromatograph	Second chromatograph
0.99–0.50	0.5–1	0.1–0.5
0.50–0.10	1–2	0.5–1
0.10–0.02	2–3	1–2
0.02–0.01	3–10	2–5
0.01–0.001	10–30	5–10
0.001–0.0001	30–100	10–20
0.0001 and lower	...	20–100[a]

[a] For the sample sizes used in this work, the limit of detectability is approximately 0.000001 mole fraction for the hydrogen flame ionization detector which is the value at which the 100% error can be expected.

The errors listed in Table I would have little effect on K values until compositions of 0.01 mole fraction and less are encountered. Otherwise sampling errors would be the cause of erratic data. Sampling problems occurred most often at low pressures with both liquid and vapor samples. In particular, the measured compositions of nitrogen and methane in the liquid phase analyses and of n-decane in the vapor phase at pressures below 1000 psia were often more erratic than expected based on the estimated precision of the chromatographic analyses.

All hydrocarbons used in this work were pure grade quality (99 mol % minimum purity). The nitrogen used had a minimum purity of 99.9 mol %, the carbon dioxide a minimum purity of 99.99 mol %, and the hydrogen sulfide a minimum purity of 99.6 mol %. These purities were specified by the suppliers and were verified by gas chromatographic and mass spectrometric analyses.

EXPERIMENTAL RESULTS

Vapor-liquid equilibrium K values were determined for nitrogen, methane, carbon dioxide, ethane, hydrogen sulfide, propane, n-pentane, n-heptane, toluene, and n-decane over a temperature range of −50–250°F and over a pressure range of 100–4500 psia. Mixtures of n-paraffin hydrocarbons both with and without the nonhydrocarbon components, and mixtures of the same n-paraffin hydrocarbons and toluene both with and without the nonhydrocarbon components were studied. Phase equilibria data were measured over a pressure range for 43 different composition and temperature conditions.

The overall mixture compositions, the experimental equilibrium phase compositions, and the K values calculated using these compositions are given in Table II (deposited with ACS Microfilm Depository Service). The equilibrium-phase analyses for Mixtures 3 through 11 were performed using the first chromatograph described. The second chromatograph was used for the analyses of equilibrium phases from Mixtures 11A through 23B and for the data measured on the system of methane and n-heptane. Total volumes, saturation pressures, and phase distribution data measured for the mixtures during constant composition equilibrium flash cell tests are reported in Table III (deposited with ACS Microfilm Depository Service). The phase equilibrium data measured on a mixture of methane and n-heptane at 0° and −40°F are given in Table IV (deposited with ACS Microfilm Depository Service.)

Figure 1. Effect of pressure on vapor-liquid equilibrium K values at 100°F

DISCUSSION OF RESULTS

Effect of Pressure on K Values. The usual effect of pressure on K values when the system temperature is such that one or more of the mixture components is above its critical temperature is well known. An example of this effect is shown at 100°F in Figure 1 for two mixtures. For the systems studied in this work the K values of all components tend to converge to a value of unity at pressures approaching the saturation pressure. However, only at the critical temperature can all the K values be unity. For systems having a bubble point or dew point, the K value versus pressure plot ends at the saturation pressure as shown in Figure 1.

Effect of Temperature on K Values. At the lower pressures (below 1000 psia for the temperatures of this study), a decrease in temperature causes the K values for all components to decrease except for those of nitrogen at temperatures above 100°F. At any pressure somewhat below the saturation pressure, the nitrogen K values reach a maximum at about 100–150°F and decrease slightly as temperature is further increased. The effect of temperature on the K values of the light and intermediate components is shown in Figures 2 and 3 for two types of mixtures, those which contained n-paraffin hydrocarbons and those which had a given concentration of
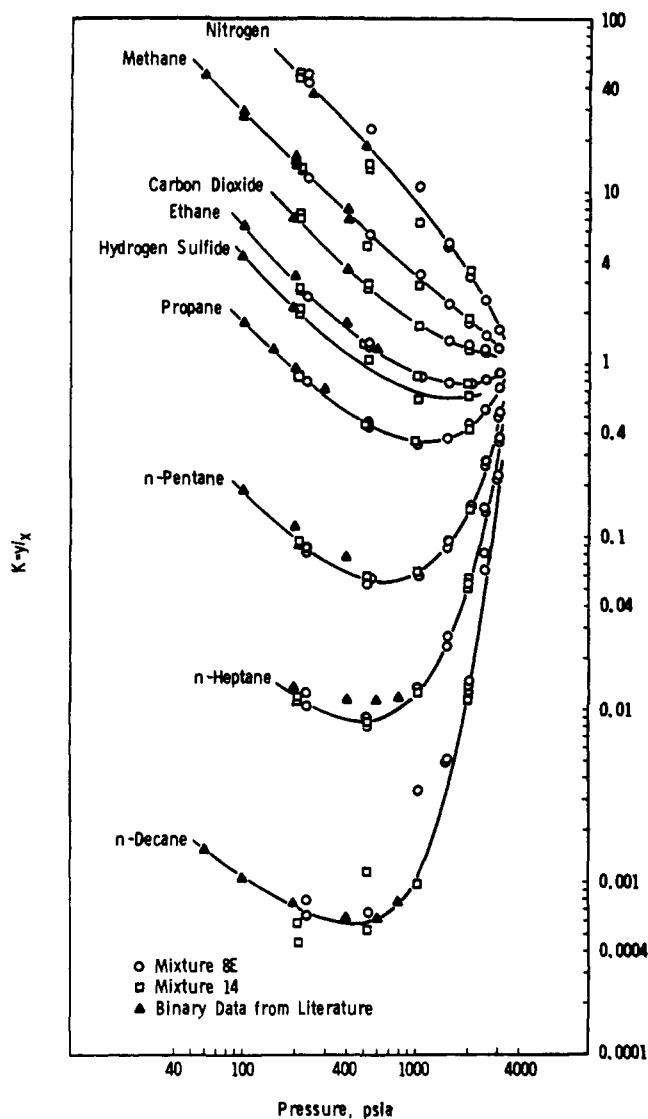
toluene added to the n-paraffin hydrocarbons. Similar effects of temperature are shown for both types of mixtures.

At pressures above 1200 psia, for the temperatures of this study, the K values of ethane and heavier components reach a minimum as temperature decreases and then increase as temperature is further decreased. An example of this behavior is shown in Figure 4.

The freezing point of n-decane is −21°F. Two mixtures in which n-decane was a component were studied at temperatures below −21°F, and solid material believed to be n-decane was observed on the windows of the cell at all pressures. Considerable n-decane was dissolved in the liquid phase and n-decane was detected in the vapor phase as would be expected.

Effect of Toluene on K Values. The addition of the aromatic component, toluene, to the mixtures containing n-paraffin hydrocarbons, in general, causes the light and intermediate hydrocarbon components and nitrogen K values to increase as shown in Figures 2 and 3. For the mixtures shown in Figures 2 and 3, the toluene composition was 64 mol % of the n-heptane, toluene, and n-decane components. The carbon dioxide K values are only slightly affected by the addition of the aromatic component. At temperatures less than 200°F, the addition of toluene causes the hydrogen sulfide K values to decrease significantly as compared to the K values in n-paraffin hydrocarbon mixtures. The magnitude of the de-
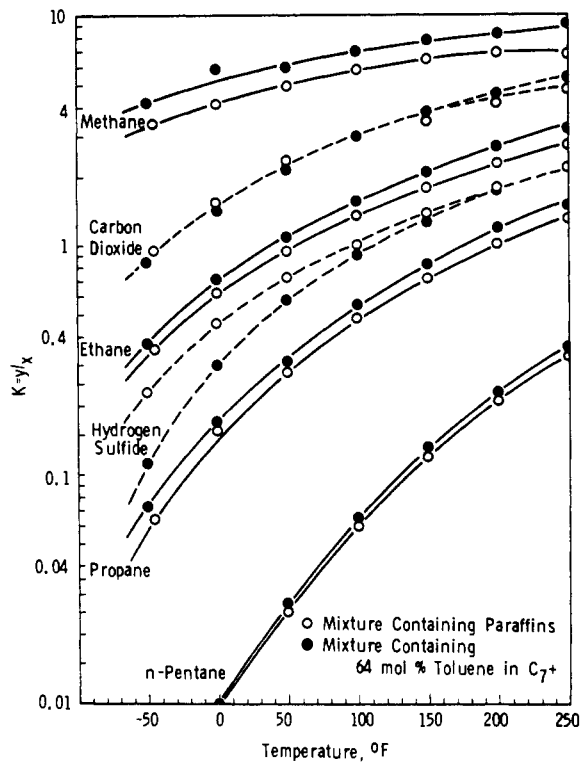
Figure 2. Effect of temperature and molecular type on vapor-liquid equilibrium K values at 500 psia
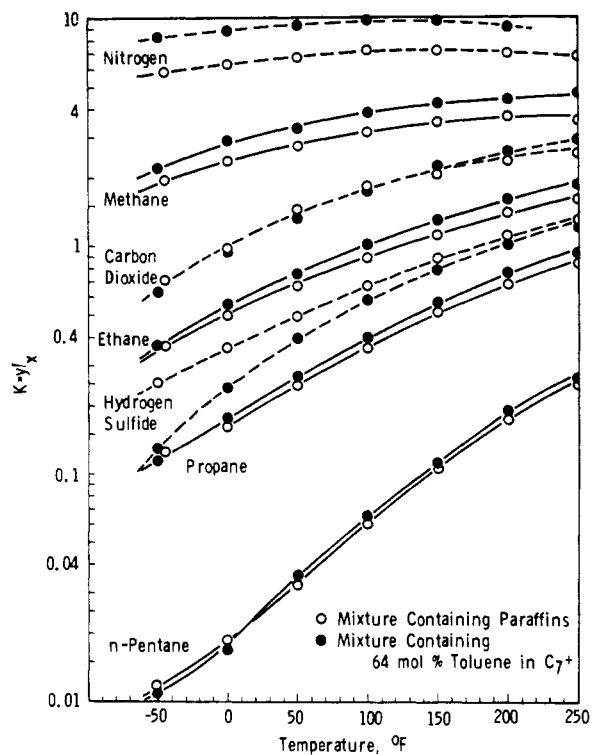

Figure 3. Effect of temperature and molecular type on vapor-liquid equilibrium K values at 1000 psia

crease depends strongly on temperature as shown in Figures 2 and 3. The lower the temperature the greater the decrease in the hydrogen sulfide K values below those shown for the systems with n-paraffin hydrocarbons.
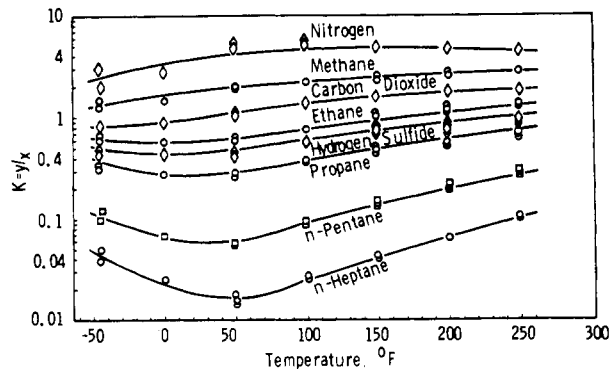
The effect of the composition of the aromatic component is

Figure 4. Effect of temperature on vapor-liquid equilibrium K values at 1530 psia
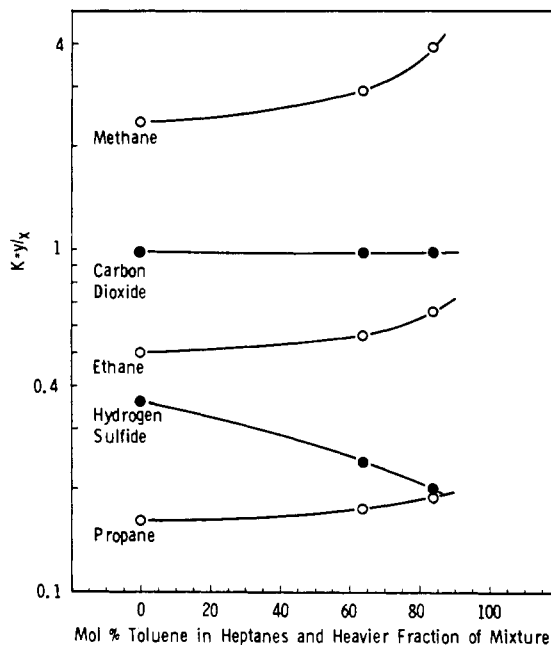

Figure 5. Effect of toluene composition in heptanes and heavier fraction on vapor-liquid equilibrium K value at 0°F and 1000 psia

shown in Figure 5 at 0°F and 1000 psia. At these conditions it appears that if enough toluene were present, the hydrogen sulfide K value could be lowered below that of propane, an unusual occurrence in a multicomponent mixture. Phase samples were removed from four mixtures used in this study at conditions where the hydrogen sulfide K value was less than the propane K value (Mixtures 15, 15B, 19, and 20B). At one set of conditions, for Mixture 15B at 0°F and 2739 psia, the hydrogen sulfide K value was less than the K values for propane, n-pentane, and n-heptane. These cases occurred when toluene was present, for temperatures of 100°F and below, and when the system pressure was approaching the saturation pressure of the mixture. This behavior indicates a strong physical attraction between molecules of hydrogen sulfide and toluene.

Effect of Nonhydrocarbons on K Values. The addition of the nonhydrocarbon components (up to 15 mol % nitrogen, 15 mol % carbon dioxide, and 25 mol % hydrogen sulfide) to the hydrocarbon mixtures generally did not affect the K values of the hydrocarbon components except at high pressures. Hydrogen sulfide was observed to have an effect on the K value of toluene at low temperatures and at pressures approaching the saturation pressure of the mixture. The nonhydrocarbons do affect the saturation pressure of a mixture and the K values

at pressures near the saturation pressure. The addition of nitrogen increased the saturation pressure while the addition of carbon dioxide and hydrogen sulfide decreased the saturation pressure of the mixtures employed in this study.

The attraction between hydrogen sulfide and toluene was mentioned previously. At temperatures below 100°F and at pressures approaching the mixture saturation pressure, hydrogen sulfide appears to lower the toluene K value with respect to the K values of the other hydrocarbon components. In one instance (Mixture 15B at 0°F and 2739 psia), the toluene K value was less than the n-decane K value.

Comparisons with Literature Data. Multicomponent n-paraffin hydrocarbon mixture K values by Vairogs et al. (14) were compared with the data measured in this study. The Vairogs et al. data were measured on a mixture which included methane, ethane, propane, n-pentane, n-hexane, and n-decane. Comparisons are shown in Figures 6 (150°F) and 7 (250°F). The two sets of K value data agree fairly well, although the data of Vairogs et al. scatter more than the data measured in this study.

K values obtained from the literature for binary mixtures containing n-paraffin hydrocarbons are shown in Figures 1, 6, and 7. Binary data for systems containing methane and n-decane (5), methane and n-heptane (10), methane and n-hexane (12), methane and n-pentane (13), methane and propane (9), ethane and n-decane (6), and propane and n-decane (8) were interpolated to obtain K values at pressures less than 1000 psia for methane, ethane, propane, n-pentane, n-hexane, n-heptane, and n-decane at 100°F, 150°F, and 250°F. The same procedure was used for nitrogen, carbon dioxide, and hydrogen sulfide at 100°F by employing data on binary systems containing nitrogen and n-hexane (4), carbon dioxide and n-decane (7), and hydrogen sulfide and n-decane (11). It was reasoned that at low pressures the composition differences between the binary and multicomponent systems would have
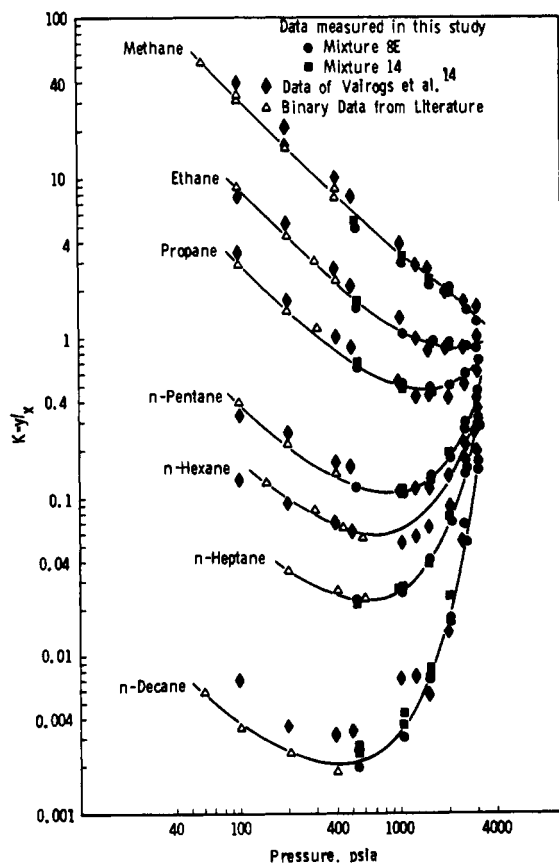
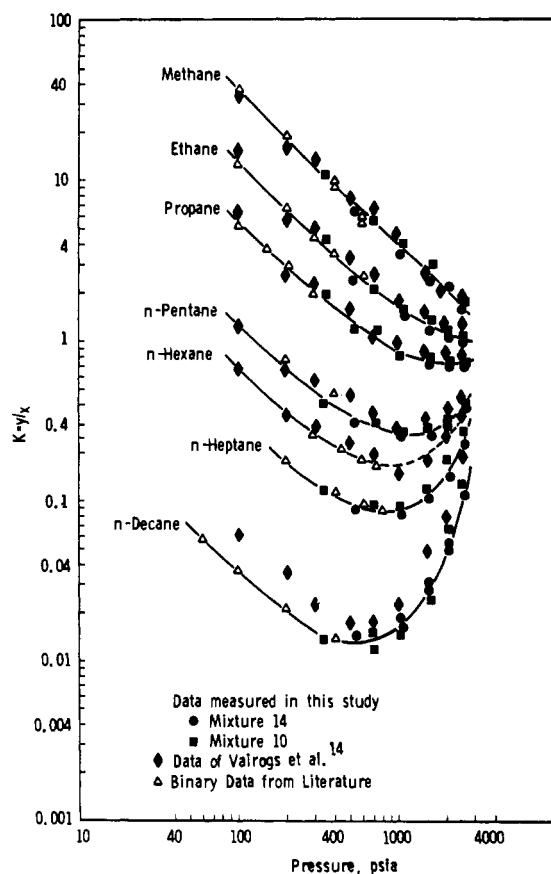Figure 7. Comparison of vapor-liquid equilibrium K values for n-paraffin hydrocarbon mixtures at 250°F

Figure 6. Comparison of vapor-liquid equilibrium K values for n-paraffin hydrocarbon mixtures at 150°F

little effect on the K values, and the binary and multicomponent data should agree. There is good agreement between the binary data and the multicomponent data obtained in this work for all components at pressures of 200 psia and less.

K values measured during this project were plotted against pressure, and smooth curves were drawn through the data similar to those shown in Figure 1. K values for n-pentane, n-heptane, toluene, and n-decane were read from the smooth curves at a pressure of 200 psia and were plotted against temperature as shown in Figure 8. For these four components the data from the binaries previously mentioned are plotted on Figure 8 as are data for a binary system containing methane and toluene at 150°F (3), the low-temperature data of Chang and coauthors for binary systems containing methane and n-heptane (1) and methane and toluene (2), and data for n-pentane in a gas-absorber oil system (15). The n-pentane and n-decane K values from all sources agree very well as shown in Figure 8. At temperatures below 100°F, the n-heptane K values from the binary systems are higher than the data measured during this study, and the discrepancy becomes greater as the temperature is lowered. At 150°F, the toluene K value from the binary system was slightly lower than the data of this study while the low-temperature binary data were considerably higher than the data of this study. As a check, phase-equilibrium data were measured at 0° and −40°F for a system containing pure-grade methane and n-heptane. Excellent agreement is shown in Figure 8 between the n-heptane K values measured during this study in the binary and multicomponent systems at 200 psia.

Another paper has been presented (16) in which a discrepancy was noted between the n-heptane K values reported by Chang et al. (1) and K values for a heptane fraction measured in a natural gas-absorber oil system. Wilson et al. (16) measured one data point on the binary system of methane and n-heptane
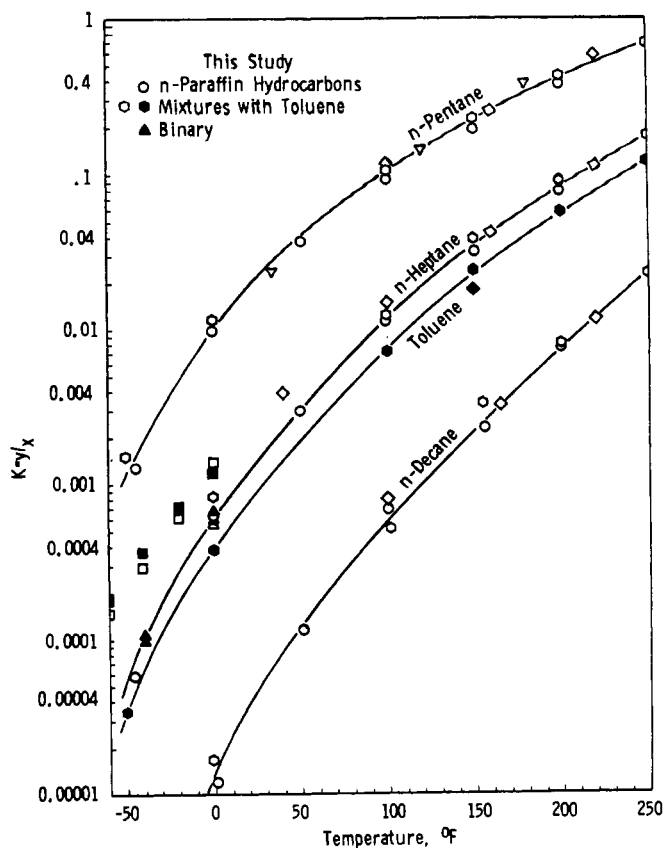
Figure 8. Comparison of vapor-liquid equilibrium K values for n-pentane and heavier components at 200 psia

◇ Sage and co-workers (5, 6, 13)
□ ■ Chang and co-workers (1, 2)
◆ Elbishlawi and Spencer (3)
△ Wilson and co-workers (16)
▽ Webber (15)

at 0°F and 200 psia, and the n-heptane K value reported and plotted in Figure 8 showed excellent agreement with the data measured in this study. The binary K values reported by Chang and co-workers for n-heptane and toluene are therefore believed to be in error at pressures less than 1000 psia.

Consistency of Data. Thermodynamic consistency tests for multicomponent vapor-liquid equilibrium data at elevated pressures are virtually nonexistent. At best, such tests would depend on calculated values of component fugacities and molar volumes of each phase, or on calculated values of component partial molar volumes and the molar volumes of each phase. Errors in estimating the information required to calculate thermodynamic consistency would invalidate the tests.

One consistency check is possible if the overall mixture composition is known in addition to the equilibrium phase compositions. This check consists of a molar balance for each component. Consistency calculations of this type have been performed for all of the phase-composition data measured during this study. The results of the calculations are good.

LITERATURE CITED

(1) Chang, H. L., Hurt, L. J., Kobayashi, R., *AIChE J.*, **12**, 1212 (1966).
(2) Chang, H. L., Kobayashi, R., *J. Chem. Eng. Data*, **12**, 517 (1967).
(3) Elbishlawi, M., Spencer, J. R., *Ind. Eng. Chem.*, **43**, 1811 (1951).
(4) Poston, R. S., McKetta, J. J., *J. Chem. Eng. Data*, **11**, 364 (1966).
(5) Reamer, H. H., Olds, R. H., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.*, **34**, 1526 (1942).
(6) Reamer, H. H., Sage, B. H., *ibid.*, **7**, 161 (1962).
(7) Reamer, H. H., Sage, B. H., *ibid.*, **8**, 508 (1963).
(8) Reamer, H. H., Sage, B. H., *ibid.*, **11**, 17 (1966).
(9) Reamer, H. H., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.*, **42**, 534 (1950).
(10) Reamer, H. H., Sage, B. H., Lacey, W. N., *J. Chem. Eng. Data*, **1**, 29 (1956).
(11) Reamer, H. H., Selleck, F. T., Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.*, **45**, 1810 (1953).
(12) Shim, J., Kohn, J. P., *J. Chem. Eng. Data*, **7**, 3 (1962).
(13) Taylor, H. S., Wald, G. W., Sage, B. H., Lacey, W. N., *Oil Gas J.*, **38**, No. 10, 46 (1939).
(14) Vairogs, J., Klekers, A. J., Edmister, W. C., *AIChE J.*, **17**, 308 (1971).
(15) Webber, C. E., *Trans. AIME*, **142**, 192 (1941).
(16) Wilson, G. M., Barton, S. T., Tullos, H. J., paper presented at 65th National Meeting of AIChE, Cleveland, Ohio, May 4–7, 1969, Paper No. 9d.
(17) Yarborough, L., Vogel, J. L., *Chem. Eng. Prog. Symp. Ser.*, **63** (81), 1 (1967).