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# Three-Phase Solid–Liquid–Vapor Equilibria of the Binary Hydrocarbon Systems Propane–Benzene, Propane–Cyclohexane, *n*-Butane–Benzene, *n*-Butane–Cyclohexane, *n*-Butane–*n*-Decane, and *n*-Butane–*n*-Dodecane

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**Pressure, temperature, liquid-phase compositions, and liquid-phase molar volumes are presented along the solid–liquid–vapor loci of six binary systems: the solvent propane with solutes benzene and cyclohexane, and the solvent *n*-butane with solutes benzene, cyclohexane, *n*-decane, and *n*-dodecane. The data were taken by using cryoscopic techniques over a liquid compositional range extended from the solute triple point to dilute solute solutions. When represented as a plot of the logarithm of solute composition vs. reduced reciprocal temperature $T_T/T$, the data are smooth curves which become linear at the low-temperature (low solute composition) end of the loci. The standard deviations of the liquid-phase solute composition data are 0.19% for the propane–benzene system, 0.47% for the propane–cyclohexane system, 0.32% for the *n*-butane–benzene system, 0.45% for the *n*-butane–cyclohexane system, 0.08% for the *n*-butane–*n*-decane system, and 2.05% for the *n*-butane–*n*-dodecane system.**

## Introduction

Solid solubility data of hydrocarbon components in low molecular weight solvents are important for use in the design of liquefaction, vaporization, and transport systems for liquefied natural gas (LNG) and liquefied petroleum gas (LPG). We have been engaged in an extended program of obtaining and classifying such data, primarily in the low solute concentration range.

In previous papers, we reported the solubility of two different hydrocarbon solutes in methane (*1*), eight different hydrocarbon solutes in ethane (*2–4*), and two different hydrocarbon solutes in propane (*4*). In this present paper, we report the solubility of six different hydrocarbon solutes in the solvent species propane and *n*-butane. All of these binary data form a basis from which the solubility of paraffinic, aromatic, and naphthenic hydrocarbons in LNG and LPG systems can be correlated and predicted.

## Experimental Section

The apparatus was identical with that described by Lee and Kohn (*5*), which was used in other cryoscopic studies (*1–3*). The experimental procedure is described in our earlier paper (*6*).

The propane and *n*-butane used in this study were Linde "instrument grade" stated to be 99.5 mol% pure. A 253.48 K isotherm determined on the propane indicated a difference between dew-point and bubble-point pressures of less than 0.1 atm. The vapor pressure and the liquid-phase molar volume at 50 vol% liquid were within 0.1 atm and 0.2 mL/(g-mol), respectively, of the literature values (*7*). The propane and *n*-butane were used without further purification.

Table I. Solid-Liquid-Vapor Three-Phase Smoothed Data for the Propane-Benzene Binary System

| temp, K | press., atm | compn[a] | molar vol,[b] mL/(g-mol) |
|---|---|---|---|
| 265 | 1.79 | 0.764 8 | 85.0 |
| 260 | 1.75 | 0.658 0 | 83.7 |
| 255 | 1.70 | 0.552 5 | 82.3 |
| 250 | 1.61 | 0.445 2 | 81.1 |
| 245 | 1.48 | 0.350 8 | 79.8 |
| 240 | 1.32 | 0.274 1 | 78.6 |
| 235 | 1.14 | 0.215 2 | 77.5 |
| 230 | 0.94 | 0.168 9 | 76.5 |
| 225 | 0.84 | 0.133 5 | 75.6 |
| 220 | 0.75 | 0.106 7 | 74.8 |
| 215 | 0.66 | 0.084 87 | 74.1 |
| 210 | 0.58 | 0.067 96 | 73.4 |
| 205 | 0.51 | 0.054 34 | 72.7 |
| 200 | 0.46 | 0.043 26 | 72.1 |
| 195 | | 0.034 55 | 71.4 |
| 190 | | 0.027 35 | 70.7 |
| 185 | | 0.021 57 | 70.0 |
| 180 | | 0.016 76 | 69.4 |
| 175 | | 0.012 83 | 68.6 |
| 170 | | 0.009 81 | 67.9 |
| 165 | | 0.007 36 | 67.4 |
| 160 | | 0.005 48 | 67.2 |

[a] Liquid phase (mole fraction benzene). [b] Liquid phase.

The *n*-decane and *n*-dodecane were Humphrey-Wilkinson "Pure Grade" petroleum-derived products with a stated purity of 99%. The benzene was a Mallinckrodt "Spectrar" spectrophotometric-grade chemical. The cyclohexane used was an Eastman Reagent "ACS Grade" chemical. The air-saturated freezing points of these hydrocarbon solutes were within ±0.1 K of the literature values, with the exception of benzene, which was within ±0.3 K. The refractive indexes differed by no more than ± 0.0003 from the literature values for all of the hydrocarbon solutes. All four solutes were used without further purification.

## Results

Tables I and II present the smoothed experimental data for the two propane solvent systems, and Tables III–VI present the smoothed experimental data for the four *n*-butane solvent systems. The pressures are precise to ±0.1 atm, the temperatures to ±0.2 K, and the liquid-phase molar volume to ±1.0 mL/(g-mol). The liquid-phase composition data were smoothed

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**Table II. Solid–Liquid–Vapor Three-Phase Smoothed Data for the Propane–Cyclohexane Binary System**

| temp, K | press., atm | compn[a] | molar vol,[b] mL/(g-mol) |
|---|---|---|---|
| 245 | 0.65 | 0.8546 | 98.9 |
| 240 | 0.64 | 0.8316 | 97.6 |
| 235 | 0.63 | 0.8086 | 96.4 |
| 230 | 0.61 | 0.7852 | 95.1 |
| 225 | 0.60 | 0.7616 | 94.0 |
| 220 | 0.58 | 0.7379 | 92.8 |
| 215 | 0.55 | 0.7144 | 91.6 |
| 210 | 0.53 | 0.6915 | 90.5 |
| 205 | 0.51 | 0.6718 | 89.5 |
| 200 | 0.48 | 0.6538 | 88.3 |
| 195 | 0.45 | 0.6304 | 87.2 |
| 190 | | 0.6056 | 86.1 |
| 185 | | 0.5801 | 83.5 |
| 180 | | 0.5114 | 81.4 |
| 175 | | 0.4114 | 79.2 |
| 170 | | 0.3302 | 77.1 |
| 165 | | 0.2641 | 75.0 |
| 160 | | 0.2083 | 72.8 |
| 156 | | 0.1658 | 71.0 |

[a] Liquid phase (mole fraction cyclohexane). [b] Liquid phase.

**Table III. Solid–Liquid–Vapor Three-Phase Smoothed Data for the *n*-Butane–Benzene Binary System**

| temp, K | press., atm | compn[a] | molar vol,[b] mL/(g-mol) |
|---|---|---|---|
| 270 | 0.60 | 0.863 7 | 88.4 |
| 265 | 0.59 | 0.780 2 | 89.2 |
| 260 | 0.58 | 0.664 0 | 89.7 |
| 255 | 0.56 | 0.550 3 | 90.0 |
| 250 | 0.55 | 0.448 4 | 90.2 |
| 245 | 0.53 | 0.360 0 | 90.2 |
| 240 | 0.51 | 0.290 0 | 90.2 |
| 235 | 0.49 | 0.230 6 | 90.1 |
| 230 | 0.47 | 0.180 9 | 89.8 |
| 225 | 0.45 | 0.146 4 | 89.3 |
| 220 | | 0.118 4 | 88.7 |
| 215 | | 0.097 36 | 87.9 |
| 210 | | 0.079 81 | 87.1 |
| 205 | | 0.065 48 | 86.1 |
| 200 | | 0.053 31 | 85.3 |
| 195 | | 0.043 12 | 84.5 |
| 190 | | 0.034 54 | 83.8 |
| 185 | | 0.027 28 | 83.2 |
| 180 | | 0.021 20 | 82.7 |
| 175 | | 0.016 49 | 82.4 |
| 170 | | 0.012 74 | 82.0 |
| 165 | | 0.009 81 | 81.7 |
| 160 | | 0.007 66 | 81.3 |

[a] Liquid phase (mole fraction benzene). [b] Liquid phase.

**Table IV. Solid–Liquid–Vapor Three-Phase Smoothed Data for the *n*-Butane–Cyclohexane Binary System[a]**

| temp, K | compn[b] | molar vol,[c] mL/(g-mol) | temp, K | compn[b] | molar vol,[c] mL/(g-mol) |
|---|---|---|---|---|---|
| 260 | 0.9630 | 108.5 | 205 | 0.6745 | 96.6 |
| 255 | 0.9329 | 107.2 | 200 | 0.6504 | 95.5 |
| 250 | 0.9059 | 106.1 | 195 | 0.6269 | 94.2 |
| 245 | 0.8787 | 105.1 | 190 | 0.6046 | 93.2 |
| 240 | 0.8522 | 104.2 | 185 | 0.5848 | 91.2 |
| 235 | 0.8260 | 103.0 | 180 | 0.4983 | 89.5 |
| 230 | 0.8004 | 102.5 | 175 | 0.3983 | 87.7 |
| 225 | 0.7749 | 101.5 | 170 | 0.3291 | 86.4 |
| 220 | 0.7497 | 100.1 | 165 | 0.2679 | 85.2 |
| 215 | 0.7246 | 99.0 | 160 | 0.2172 | 84.2 |
| 210 | 0.6995 | 97.7 | 157 | 0.1864 | 83.7 |

[a] Pressure is less than 0.45 atm at all data points. [b] Liquid phase (mole fraction cyclohexane). [c] Liquid phase.

**Table V. Solid–Liquid–Vapor Three-Phase Smoothed Data for the *n*-Butane–*n*-Decane Binary System[a]**

| temp, K | compn[b] | molar vol,[c] mL/(g-mol) | temp, K | compn[b] | molar vol,[c] mL/(g-mol) |
|---|---|---|---|---|---|
| 240 | 0.8156 | 166.5 | 200 | 0.048 13 | 90.0 |
| 235 | 0.6008 | 143.5 | 195 | 0.031 61 | 88.0 |
| 230 | 0.4371 | 128.6 | 190 | 0.020 43 | 86.6 |
| 225 | 0.3140 | 117.5 | 185 | 0.012 99 | 85.6 |
| 220 | 0.2224 | 109.0 | 180 | 0.008 15 | 84.6 |
| 215 | 0.1551 | 102.4 | 175 | 0.005 08 | 83.9 |
| 210 | 0.1066 | 97.2 | 170 | 0.003 17 | 83.0 |
| 205 | 0.07220 | 93.2 | 165 | 0.001 99 | 82.5 |

[a] Pressure is less than 0.45 atm at all data points. [b] Liquid phase (mole fraction *n*-decane). [c] Liquid phase.

**Table VI. Solid–Liquid–Vapor Three-Phase Smoothed Data for the *n*-Butane–*n*-Dodecane Binary System[a]**

| temp, K | compn[b] | molar vol,[c] mL/(g-mol) | temp, K | compn[b] | molar vol,[c] mL/(g-mol) |
|---|---|---|---|---|---|
| 255 | 0.5795 | 163.5 | 215 | 0.024 61 | 91.1 |
| 250 | 0.4125 | 141.5 | 210 | 0.015 41 | 88.9 |
| 245 | 0.2886 | 126.0 | 205 | 0.009 54 | 87.5 |
| 240 | 0.1987 | 115.0 | 200 | 0.005 82 | 86.3 |
| 235 | 0.1345 | 107.2 | 195 | 0.003 50 | 85.2 |
| 230 | 0.08985 | 101.2 | 190 | 0.002 06 | 84.5 |
| 225 | 0.05914 | 96.6 | 185 | 0.001 24 | 83.9 |
| 220 | 0.03836 | 93.0 | | | |

[a] Pressure is less than 0.45 atm at all data points. [b] Liquid phase (mole fraction *n*-dodecane). [c] Liquid phase.

**Table VII. Standard Deviation for Liquid-Phase Solute Compositions, Total Number of Data Points, and Number of Cell Loadings for the Six Binary Systems Studied**

| system | SD, % | no. of data points | no. of cell loadings |
|---|---|---|---|
| propane–benzene | 0.19 | 39 | 6 |
| propane–cyclohexane | 0.47 | 19 | 2 |
| *n*-butane–benzene | 0.32 | 47 | 5 |
| *n*-butane–cyclohexane | 0.45 | 38 | 2 |
| *n*-butane–*n*-decane | 0.08 | 44 | 6 |
| *n*-butane–*n*-dodecane | 2.05 | 51 | 6 |

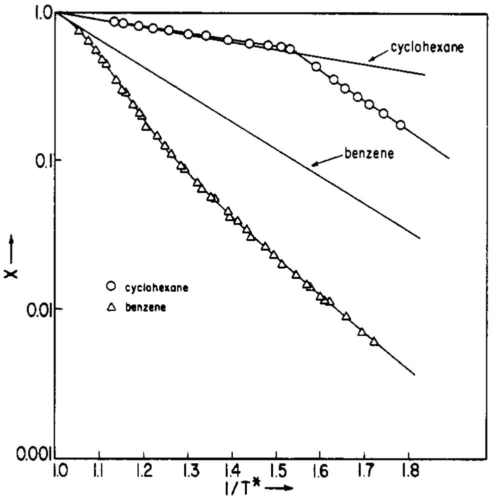

**Figure 1.** Experimental solute mole fraction vs. reduced reciprocal temperature as compared with ideal predictions for the systems propane–benzene and propane–cyclohexane. The heavy lines are the smoothed data presented in Tables I and II, while the light lines are the ideal solubility loci for both systems.

before tabulation by use of the same procedure reported earlier (*2*, *3*). Table VII gives the standard deviation between

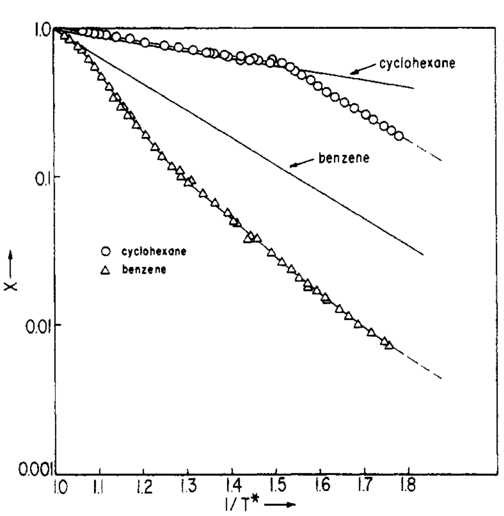

**Figure 2.** Experimental solute mole fraction vs. reduced reciprocal temperatures as compared with ideal predictions for the system *n*-butane–benzene and *n*-butane–cyclohexane. The heavy lines are the smoothed data presented in Tables III and IV, while the light lines are the ideal solubility loci for both systems.

smoothed and raw data, as well as the number of cell loadings and data points taken.

The raw data and the smoothed composition lines for the first four systems are presented in Figures 1 and 2. The straight lines on these semilogarithmic plots are "ideal" solubility lines. At high values of $1/T^*$, the data start to become linear in these coordinates, a characteristic observed in our earlier studies and interpreted as the region in which Henry's law for dilute solutions might be expected to be valid. It is felt that linear extrapolation of these data in these semilogarithmic plots would be reasonably accurate. All raw data are available as suplementary material. (See paragraph at end of text regarding supplementary material.)

No plot is presented of the data for the systems *n*-butane–*n*-decane and *n*-butane–*n*-dodecane, as the compositions of these two systems are quite close to those which would be predicted by "ideal" solubility.

All of the S–L–V loci presented herein are continuous from solute triple point to dilute solute region, as the molecular differences between the solute and the solvent are not severe. The nearly "ideal" behavior in the systems *n*-butane with *n*-decane and *n*-dodecane is not surprising if one recalls the near"ideal" behavior of the systems propane and these same solutes (*7*). Looking at these solutes and the solubility behavior in ethane (*2*, *3*), propane, and butane, one notes that the solute composition increases with solvent molecule size at a given temperature. The same effect is noted with the solute benzene; however, along a portion of the *n*-butane–cyclohexane locus, the solute composition values are less than their corresponding values on the propane–cyclohexane locus.

From examination of the data herein and earlier data on *n*-paraffin solutes, one can suggest that nonideality is significant with the solvent ethane for *n*-paraffin solutes above *n*-octane, and with the solvent propane for solutes above *n*-decane, while the solvent *n*-butane is ideal for solutes up to *n*-dodecane.

## Glossary

| | |
|---|---|
| L | liquid phase |
| S | solid phase |
| $T$ | temperature in K |
| $T_T$ | triple-point temperature in K: 278.69 K for benzene, 279.83 K for cyclohexane, 243.51 K for *n*-decane, and 263.61 K for *n*-dodecane |
| $T^*$ | $T/T_T$ |
| $x$ | solute mole fraction in phase L |

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**Supplementary Material Available:** Complete tables of raw data for all six binary systems (8 pages). Ordering information is given on any current masthead page.

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# Viscosities and Densities of Four Binary Liquid Systems at 25.00 °C

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**Densities and viscosities of four binary systems, viz., benzene–toluene, chloroform–toluene, chloroform–benzene, and benzene–*n*-hexane, have been determined at 25.00 °C, over the complete composition ranges. The results have been discussed in the light of ideal solution behavior. A few of the existing predictive equations of mixture viscosities have been tested.**

## Introduction

The ideal mixture concept, widely used in solution thermodynamics, corresponds to a limiting behavior that has a physical basis in the properties of highly dilute solutions, but may lack such basis in the case where the ideal mixture concept is extended to cover the entire mole fraction range of a liquid system. Presented in this paper are results of density and viscosity determinations on carefully selected binary liquid mixtures, such that could be expected to approximate ideal solution behavior as closely as any liquid system of chemically different components may.

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