

-60 and 50° F. For each experimental-liquid composition and temperature, the corresponding pressure and vapor composition were back calculated using the correlation as given in Equations 1, 2, and 4-8. (Equations 7 and 8, which represent the temperature correlation of the Λ 's, are considered to be the correlation rather than the Λ values from Table III, which are the best Λ 's for each isotherm independent of the others.) The results of this calculation for 50° F are superimposed on the experimental data in Figure 1.

The overall average absolute difference between experimental and calculated pressures was 0.6%. Calculated vapor compositions had a root-mean-square difference of 0.005 mole fraction from the experimental compositions. The correlation fits the isotherms of 50, 20, and -20° F equally well with an average absolute difference between experimental and calculated pressures of 0.4%; the maximum deviation was about 1% on each of these isotherms. (At these maximums, the deviations in terms of pressure differences were 3.2, 2.7, and 0.8 psia, respectively.) The poorest fit was for -60° F where the average deviation was 1.1% with a maximum difference of 3.3% which corresponded to 1.0 psia. With respect to calculated vapor compositions for a given liquid composition and temperature, the best fit was for -20° F where the root-mean-square difference between calculated and experimental composition was 0.004; the poorest fit was for -60° F where the root-mean-square difference was 0.007.

ACKNOWLEDGMENT

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NOMENCLATURE

| | |
|------------|--|
| a, b | = constants in the Redlich-Kwong equation of state |
| f_i^{oL} | = liquid-phase standard-state fugacity, psia |
| k_{ij} | = binary interaction constant |
| P | = system pressure, psia |
| P^s | = vapor (saturation) pressure, psia |
| R | = gas constant, 10.73 psia cu ft/lb mole ° R |
| t | = temperature, ° F |
| T | = temperature, ° R |

| | |
|-------|---|
| v | = molar volume of vapor phase, cu ft/lb mole |
| v^L | = molar volume of liquid phase, cu ft/lb mole |
| x | = liquid-phase mole fraction |
| y | = vapor-phase mole fraction |

Greek Letters

| | |
|---------------------------------|--|
| $\Lambda_{ij}, \Lambda_{ji}$ | = parameters in the Wilson equation |
| $(\lambda_{ij} - \lambda_{ji})$ | = energy-difference term in the Wilson equation, Btu/lb mole |
| ϕ | = vapor-phase fugacity coefficient |
| ϕ^s | = fugacity coefficient of pure saturated vapor |
| Ω_c, Ω_b | = dimensionless constants in the Redlich-Kwong equation of state |

Subscripts

| | |
|-----|-----------------|
| i | = component i |
| j | = component j |
| k | = component k |

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Vapor-Liquid Equilibria in Binary Aromatic-Olefin Systems

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The thermodynamic properties of mixtures of normal and branched paraffins with aromatics have been discussed recently (4, 5).

For mixtures of olefins with aromatics there are very few experimental results. Only data for three systems have been previously reported: benzene-cyclohexene (2) (25°, 50°, and 75° C); ethylbenzene-octene-1 (28) (760 mm Hg); and naphthalene-hexadecene-1 (27) (200 mm Hg).

For rational design of distillation equipment and for fundamental understanding of the effect of molecular structure on thermodynamic properties, we require additional vapor-liquid equilibrium data for aromatic-olefin systems.

In this work, isothermal, low-pressure vapor-liquid equilibrium data are reported in the temperature range 10° to 50° C for five binary systems: benzene-hexene-1; benzene-2-methylpentene-1; benzene-4-methylpentene-1; benzene-octene-1; and toluene-hexene-1.

The new data and those previously published are reduced to yield thermodynamic excess functions.

EXPERIMENTAL

Total vapor pressures for the five systems studied were measured as a function of composition at constant temperature. The static method was used. A detailed discussion of the advantages and disadvantages of this method has been given previously by Scatchard (23).

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Isothermal vapor-pressure data over the whole range of composition were obtained for five binary systems: benzene-hexene-1; benzene-2-methylpentene-1; benzene-4-methylpentene-1; benzene-octene-1; and toluene-hexene-1 in the range 10° to 50° C. Excess Gibbs energies were calculated for these systems and for two binary aromatic-olefin systems previously reported in the literature. All of these systems exhibit only small positive deviations from Raoult's law. Excess enthalpies at 25° C for the midpoint composition are reported for the five measured systems.

Pure components of the highest purity commercially available were used. Benzene and toluene from Matheson, Coleman and Bell were more than 99.9% pure. All olefins were supplied by Phillips Petroleum Co. Hexene-1 and 2-methylpentene-1 were more than 99.9% pure and octene-1 and 4-methylpentene-1 were more than 99.8% pure. The pure liquids were dried over Linde molecular sieves and were used without further purification. Only trace impurities were detected by gas-solid chromatographic analysis.

Mixture compositions were determined from measurements of index of refraction using a Bausch-and-Lomb refractometer thermostated at 25° C. Calibration plots of index of refraction vs. composition were prepared for each binary system.

The apparatus is shown schematically in Figure 1; it is essentially the same as that described by Hermesen (8) and Orye (16) with modifications introduced by Harris (7).

The pure components were sealed in separate stills for degassing. The air was removed by freezing the pure components with liquid nitrogen and opening the stills to the vacuum system while they were melting under vigorous agitation by a magnetic stirrer. Upon repeating this operation several times the components were completely degassed. Degassing was considered complete when a thermocouple vacuum gage located in the vacuum line did not detect any air at the time of opening the still with the frozen component. As a further check to assure complete degassing the pure-component vapor pressure was measured, as indicated below, and its value was compared with the literature (22, 25).

Each component was transferred to the equilibrium cell by distilling from the degassing stills and condensing in the equilibrium cell with liquid nitrogen. The cell was then gradually warmed and thermostated at the desired temperature within $\pm 0.01^\circ$ C. The small null manometer was balanced approximately by bleeding air into its reference side through a needle valve.

To assure uniform temperature and composition, the mixture in the cell was under continuous agitation by a magnetic stirrer. When equilibrium was attained, about 40 min after the desired temperature was established, the vapor pressure of the mixture was measured with a Texas

Instruments fused-quartz pressure gage. Null manometer imbalance was measured with a Wild-Heerbrugg cathetometer. An auxiliary mercury manometer was used for periodic calibrations of the fused-quartz pressure gage. The vapor-pressure measurements were reduced to millimeters of mercury at 0° C and standard gravity. Measured temperatures are estimated to be accurate to $\pm 0.05^\circ$ C.

After the vapor pressure was measured at different temperatures, the sample was completely transferred from the equilibrium cell to a collection cell previously evacuated and cooled with liquid nitrogen. The thermocouple vacuum gage of the vacuum line indicated when the transfer was completed.

Samples were analyzed by refractive-index measurements in triplicate. Even though analysis of known samples indicates a maximum error of only about ± 0.001 mole fraction, in most cases the largest experimental error was associated with this analysis.

If we consider the effect of interpolation on the index-of-refraction calibration curve to find the sample composition, the mentioned uncertainties in temperature and in refractive index, and a maximum error of 0.10 mm of mercury in measuring the pressure, the experimental vapor pressures are accurate to better than $\pm 0.50\%$ at each temperature.

Detailed experimental results are given in Table I.

Special experimental problems were found when working with octene-1. Frequently, when the sample was in the equilibrium cell, the normally colorless liquid darkened. A similar experience has been reported by Larkin et al. (11) working with 2-methylpentane and was thought to be due to peroxide formation (17) when the hydrocarbon is in contact with mercury. The same explanation is probably valid for octene-1 since the vapor of the sample is in contact with the mercury of the null manometer, and the small amount of impurities present can lead to some peroxide formation. As this contact is unavoidable in the apparatus used in the present work, the complication was overcome by cleaning the equilibrium cell each time that the dark color appeared. Also, before preparing each mixture in the equilibrium cell, the pure-component vapor pressure of octene-1 at 10° C was measured and compared with the accepted value at this temperature (22). (When the sample was slightly dark the vapor pressure was somewhat lower.)

DATA REDUCTION

Vapor-pressure data over the whole range of composition were reduced to calculate the excess Gibbs energy by a computational method described previously (20).

For a binary mixture the molar excess Gibbs energy g^E depends on the liquid mole numbers n_1 and n_2

$$(n_1 + n_2)g^E = f(A, B, C, \dots, n_1, n_2) \quad (1)$$

where A, B, C, \dots are adjustable parameters, constant for each temperature and independent of composition (9, 10, 19). The form of the function, f , is arbitrary, except that it must satisfy the boundary conditions: $f = 0$ when $n_1 = 0$ and when $n_2 = 0$. Once the form of this function is assumed, the activity coefficient, γ_i , can be computed according to the exact expression:

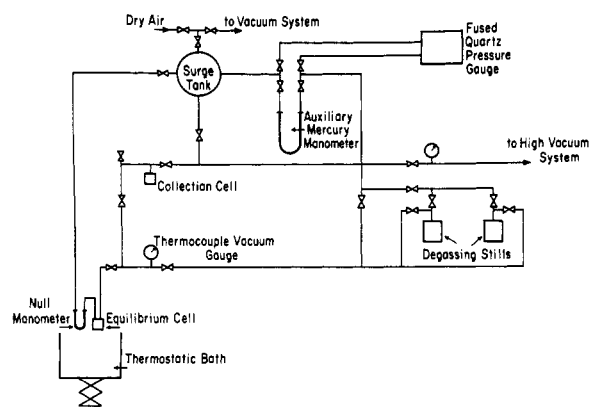


Figure 1. Schematic view of the apparatus

Table I. Experimental Results

| Aromatic mole fraction in liquid | Total pressure in mm Hg std | | |
|----------------------------------|-----------------------------|--------|--------|
| | 10° C | 30° C | 50° C |
| Benzene-hexene-1 | | | |
| 0.000 | 94.84 | 228.94 | 485.30 |
| 0.162 | 91.55 | 219.61 | 466.52 |
| 0.261 | 87.88 | 212.33 | 453.42 |
| 0.410 | 81.81 | 198.00 | 426.26 |
| 0.474 | 79.28 | 191.49 | 414.22 |
| 0.597 | 73.68 | 179.76 | 390.15 |
| 0.758 | 65.93 | 162.35 | 352.96 |
| 0.858 | 58.96 | 147.60 | 325.09 |
| 0.931 | 53.34 | 136.13 | 301.26 |
| 1.000 | 45.53 | 119.34 | 271.29 |
| Benzene-2-methylpentene-1 | | | |
| 0.000 | 99.87 | 240.07 | 507.90 |
| 0.066 | 98.15 | 235.35 | 498.40 |
| 0.226 | 92.40 | 222.63 | 473.82 |
| 0.302 | 89.24 | 216.19 | 461.20 |
| 0.429 | 84.50 | 203.75 | 435.20 |
| 0.510 | 80.46 | 195.38 | 418.67 |
| 0.672 | 72.77 | 176.62 | 381.54 |
| 0.828 | 62.37 | 155.22 | 339.10 |
| 0.955 | 50.74 | 130.90 | 292.53 |
| Benzene-4-methylpentene-1 | | | |
| 0.000 | 143.58 | 329.15 | 670.13 |
| 0.086 | 136.20 | 313.47 | 641.55 |
| 0.247 | 124.46 | 288.75 | 593.46 |
| 0.320 | 120.04 | 278.70 | 573.96 |
| 0.435 | 110.43 | 258.38 | 534.35 |
| 0.541 | 102.35 | 239.84 | 498.47 |
| 0.666 | 91.22 | 215.04 | 450.24 |
| 0.814 | 74.97 | 180.37 | 384.17 |
| 0.895 | 63.97 | 156.91 | 339.55 |
| Benzene-octene-1 | | | |
| 0.000 | 7.21 | 22.77 | 60.49 |
| 0.165 | 15.52 | 43.15 | 103.53 |
| 0.265 | 20.17 | 54.12 | 126.81 |
| 0.411 | 26.29 | 69.67 | 160.18 |
| 0.533 | 31.14 | 81.30 | 185.36 |
| 0.602 | 33.63 | 88.01 | 200.39 |
| 0.661 | 35.17 | 92.18 | 210.64 |
| 0.824 | 40.77 | 105.86 | 240.70 |
| 0.887 | 42.09 | 110.32 | 250.75 |
| Toluene-hexene-1 | | | |
| 0.209 | 79.61 | 192.10 | 409.43 |
| 0.442 | 61.91 | 152.30 | 325.67 |
| 0.562 | 52.71 | 129.78 | 280.59 |
| 0.627 | 47.77 | 117.77 | 256.09 |
| 0.683 | 43.37 | 107.24 | 233.77 |
| 0.852 | 28.04 | 72.04 | 163.57 |
| 1.000 | 12.43 | 36.64 | 92.11 |

Table II. Pure-Component Properties

| | Physical constants | | |
|-------------------|--------------------|-------------------|---------------------------|
| | T_c , °K | P_c , atm | Acentric factor, ω |
| Benzene | 562.0 (20) | 48.6 (20) | 0.211 (20) |
| Toluene | 594.0 (20) | 40.0 (20) | 0.241 (20) |
| Ethylbenzene | 619.6 ^a | 38.1 ^a | 0.315 ^b |
| Naphthalene | 748.0 (6) | 40.6 (6) | 0.314 ^b |
| Hexene-1 | 504.2 (6) | 31.1 (6) | 0.281 ^b |
| 2-Methylpentene-1 | 511.9 ^a | 31.1 ^a | 0.198 ^b |
| 4-Methylpentene-1 | 493.3 ^a | 31.8 ^a | 0.263 ^b |
| Cyclohexene | 560.4 (1) | 42.9 ^a | 0.210 (1) |
| Octene-1 | 578.2 (6) | 25.5 (6) | 0.286 ^b |
| Hexadecene-1 | 712.0 ^a | 14.7 ^a | 0.808 ^b |

^a Calculated by Lydersen's method (13). ^b Calculated from vapor-pressure data (22).

where for a component i , x_i is the mole fraction in the liquid phase, ϕ_i is the vapor-phase fugacity coefficient, and f_i^0 is the fugacity of the pure liquid at the system temperature and pressure P .

The pure liquid fugacity is given by:

$$f_i^0 = P_i^s \phi_i^s \exp [v_i(P - P_i^s)/RT] \quad (4)$$

where P_i^s is the saturation vapor pressure of the component i at the system temperature T , ϕ_i^s is its fugacity coefficient at saturation, and the exponential is the Poynting correction when the liquid phase is regarded as incompressible.

The fugacity coefficient of component i in the gas mixture was calculated from the relation (19):

$$\ln \phi_i = \frac{2}{v} \sum_{j=1}^2 y_j B_{ij} - \ln z \quad (5)$$

where v is the molar volume of the vapor mixture, z is the compressibility factor of that mixture, and B_{ij} is the second virial coefficient for the ij pair. For pure components ($i = j$) B_{ii} can be obtained from generalized correlations; the cross second virial coefficient B_{ij} ($i \neq j$) can be obtained from the same correlations by using mixing rules for the parameters as discussed previously (19). For α -olefins, a correlation has been given by McGlashan (14, 15), and a generalized correlation has been presented by Pitzer and Curl (18). Results obtained with each of these correlations together with results obtained neglecting vapor-phase corrections are given in the next section.

The fugacity coefficients at saturation were calculated from Lyckman's correlation (12) for reduced temperatures higher than 0.56 and from Equation 5 for lower reduced temperatures.

The vapor-phase composition can be calculated by

$$y_i = \frac{x_i \gamma_i f_i^0}{P_{\text{calcd}} \phi_i} \quad (6)$$

By means of an iterative calculation using Equations 1 to 6, the parameters A , B , C , ... were obtained by minimizing at each temperature

$$M^2 = \frac{1}{N-L} \sum_{i=1}^N \left[\left(\frac{P_{\text{exp}} - P_{\text{calcd}}}{P_{\text{exp}}} \right) 100 \right]^2 \quad (7)$$

where N is the number of experimental points and L is the number of adjustable parameters (A , B , C , ...) in either the Wilson equation or the Redlich-Kister equation.

Once the excess Gibbs energy is known as a function of temperature for a given composition, the excess enthalpy can be found from the exact relation (19):

$$RT \ln \gamma_i = \left[\frac{\partial(n_1 + n_2)g^E}{\partial n_i} \right]_{T,P,n_j \neq i} \quad (2)$$

where R is the gas constant and T is the absolute temperature. In this work, for the function, f , we use the Wilson equation or the Redlich-Kister equation.

A calculated total pressure of the binary mixture can be obtained from:

$$P_{\text{calcd}} = \frac{x_1 \gamma_1 f_1^0}{\phi_1} + \frac{x_2 \gamma_2 f_2^0}{\phi_2} \quad (3)$$

$$h^E = \left[\frac{\partial(g^E/T)}{\partial(1/T)} \right]_{P,x} \quad (8)$$

No calorimetric enthalpy data are available for the systems studied here.

Pure-component properties used for the calculations are given in Table II.

RESULTS

The measured total pressures were fitted first, using the Wilson two-parameter equation (19, 29):

$$g^E/RT = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(x_2 + \Lambda_{21}x_1) \quad (9)$$

and second, using the Redlich-Kister three-parameter equation (21)

$$g^E/RT = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2] \quad (10)$$

Table III gives the Wilson parameters and Table IV the Redlich-Kister parameters for the five systems at 10°, 30°, and 50° C. The two-parameter Wilson equation gives a fit to the pressure which is as good as that given by the three-parameter Redlich-Kister equation. Typical values of M for both fittings are of the order of 0.5.

Table V shows a comparison of the values of the excess Gibbs energy obtained with both equations for the system benzene-hexene-1 at 50° C. Within experimental error there is no difference.

Table VI gives for all the five measured systems the values of the midpoint composition excess Gibbs energies at 10°, 30°, and 50° C. Also, the calculated values of the excess enthalpy h^E at 25° C for the midpoint composition are reported here. Since the uncertainty in the excess Gibbs energy at the midpoint composition is approximately ± 2 cal/gmol, the uncertainty in the excess enthalpy is approximately ± 30 cal/gmol.

All results shown in Tables III through VI are based on the Pitzer-Curl (18) generalized correlation for second virial coefficients.

To study the influence of vapor-phase nonidealities, the second virial coefficients predicted by the Pitzer-Curl cor-

relation were compared with predictions based on McGlashan's correlation for normal alkanes and α -olefins. In addition to critical data, McGlashan's correlation requires a parameter, n , equal to the number of carbon atoms per molecule. However, for aromatics the parameter n is not defined. By use of a least-squares fit of experimental second virial coefficients (3) to McGlashan's equation, n was set equal to 4 for benzene and 5.5 for toluene. For the aromatics and α -olefins used here, individual second virial coefficients evaluated by both methods are reported in Table VII. Cross second virial coefficients and $\Delta = 2B_{12} - B_{11} - B_{22}$ are given in Table VIII.

Table IX shows a comparison of the excess Gibbs energy at 30° C for the system benzene-hexene-1 calculated with and without vapor-phase corrections. The differences are very small.

Included in Tables III and IV are results for the systems benzene-cyclohexene at 25°, 50°, and 75° C (2) and ethylbenzene-octene-1 (28) at 760 mm Hg. The Redlich-Kister parameters for the system benzene-cyclohexene are those reported in the original paper (2). The Wilson parameters were obtained by smoothing the data and using the pure-component vapor pressures measured in the same work.

Table IV. Redlich-Kister Parameters for Excess Gibbs Energy

$$g^E/RT = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2]$$

Component 1: aromatic. Component 2: olefin

| System | T, °C | A | B | C |
|-----------------------------------|------------------|--------|---------|---------|
| Benzene-hexene-1 | 10 | 0.4619 | 0.0460 | 0.1560 |
| | 30 | 0.3730 | 0.0469 | 0.1416 |
| | 50 | 0.3480 | 0.0477 | 0.1202 |
| Benzene-2-methylpentene-1 | 10 | 0.4674 | 0.0623 | 0.0099 |
| | 30 | 0.3953 | 0.0552 | 0.1042 |
| | 50 | 0.3520 | 0.0504 | 0.1173 |
| Benzene-4-methylpentene-1 | 10 | 0.4978 | 0.0619 | 0.0003 |
| | 30 | 0.4318 | 0.0551 | 0.0015 |
| | 50 | 0.3891 | 0.0504 | 0.0030 |
| Benzene-octene-1 | 10 | 0.3882 | 0.1521 | 0.0900 |
| | 30 | 0.3203 | 0.1029 | 0.0972 |
| | 50 | 0.2786 | 0.0908 | 0.0992 |
| Toluene-hexene-1 | 10 | 0.3119 | -0.0094 | 0.0290 |
| | 30 | 0.2801 | -0.0049 | 0.0330 |
| | 50 | 0.2501 | -0.0015 | 0.0367 |
| Benzene-cyclohexene | 25 | 0.2390 | 0.0168 | -0.0062 |
| | 50 | 0.1959 | 0.0099 | 0.0062 |
| | 75 | 0.1599 | 0.0083 | 0.0117 |
| Ethylbenzene-octene-1 (760 mm Hg) | Range 120 to 135 | 0.1324 | 0.0057 | -0.0150 |

Table III. Wilson Parameters for Excess Gibbs Energy

$$g^E/RT = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(x_2 + \Lambda_{21}x_1)$$

Component 1: aromatic. Component 2: olefin

| System | T, °C | Λ_{12} | Λ_{21} |
|-----------------------------------|------------------|----------------|----------------|
| Benzene-hexene-1 | 10 | 1.0095 | 0.5648 |
| | 30 | 1.0978 | 0.5656 |
| | 50 | 1.1251 | 0.5684 |
| Benzene-2-methylpentene-1 | 10 | 1.0086 | 0.5764 |
| | 30 | 1.0614 | 0.5821 |
| | 50 | 1.0931 | 0.5902 |
| Benzene-4-methylpentene-1 | 10 | 0.9761 | 0.5787 |
| | 30 | 1.0168 | 0.5983 |
| | 50 | 1.0324 | 0.6191 |
| Benzene-octene-1 | 10 | 1.5199 | 0.3097 |
| | 30 | 1.5288 | 0.3491 |
| | 50 | 1.5366 | 0.3735 |
| Toluene-hexene-1 | 10 | 0.7880 | 0.9095 |
| | 30 | 0.8327 | 0.8996 |
| | 50 | 0.8849 | 0.8737 |
| Benzene-cyclohexene | 25 | 0.8844 | 0.8710 |
| | 50 | 0.9231 | 0.8409 |
| | 75 | 1.1914 | 0.6622 |
| Ethylbenzene-octene-1 (760 mm Hg) | Range 120 to 135 | 0.9679 | 0.8989 |

Table V. Comparison of Excess Gibbs Energy for System Benzene-Hexene-1 at 50° C Obtained with Equation 9 and with Equation 10

| Aromatic mole fraction in liquid | g^E , cal/gmol | |
|----------------------------------|------------------|-------------|
| | Equation 9 | Equation 10 |
| 0.162 | 28.63 | 32.28 |
| 0.261 | 41.90 | 43.63 |
| 0.410 | 55.03 | 53.26 |
| 0.474 | 57.91 | 55.29 |
| 0.597 | 58.25 | 55.81 |
| 0.758 | 47.06 | 47.60 |
| 0.858 | 32.48 | 34.68 |
| 0.931 | 17.63 | 19.72 |

The data for the system naphthalene-hexadecene-1 (27) appear to be poor and when reduced give negative deviations from Raoult's law.

DISCUSSION

Binary aromatic-olefin systems are much more ideal than similar aromatic-paraffin systems. To illustrate, Figure 2 shows a comparison of the excess Gibbs energies of the systems benzene-cyclohexane (24) and benzene-cyclohexene

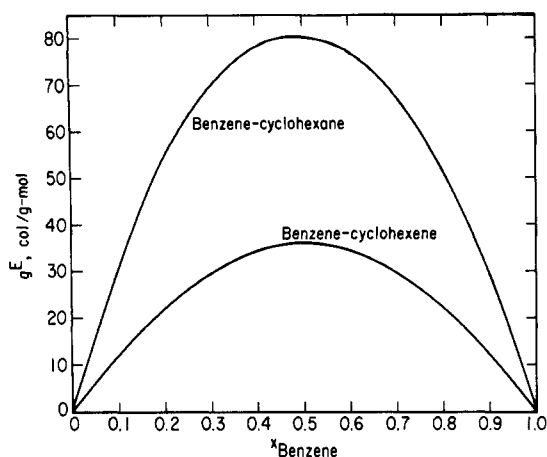


Figure 2. Excess Gibbs energies at 25°C for the systems benzene-cyclohexane and benzene-cyclohexene

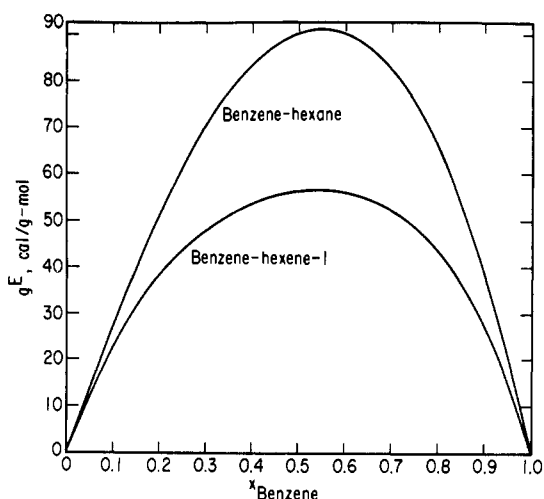


Figure 3. Excess Gibbs energies at 30°C for the systems benzene-hexane and benzene-hexene-1

Table VI. Excess Thermodynamic Properties at Midpoint Composition ($x = 0.5$)

| System | $g_x^E, \text{cal/gmol}$ | | | $h_x^E, \text{cal/gmol}, 25^\circ\text{C}$ |
|---------------------------|--------------------------|-------|-------|--|
| | 10°C | 30°C | 50°C | |
| Benzene-hexene-1 | 64.97 | 56.18 | 55.87 | 148 |
| Benzene-2-methylpentene-1 | 65.75 | 59.53 | 56.52 | 143 |
| Benzene-4-methylpentene-1 | 70.03 | 65.03 | 62.48 | 135 |
| Benzene-octene-1 | 54.60 | 48.24 | 44.73 | 133 |
| Toluene-hexene-1 | 43.87 | 42.19 | 40.16 | 70 |

(2) at 25°C. Figure 3 shows the same comparison for the systems benzene-hexane (26) and benzene-hexene-1 at 30°C.

The results for benzene-hexene-1 and those for toluene-hexene-1 (Table VI) show that, as expected, the methyl group of toluene makes the second system more ideal than the first.

Tables VII and VIII indicate that the second virial coefficients and related quantities calculated with the Pitzer-Curl correlation are not significantly different from those calculated with McGlashan's correlation. Further, Table IX shows that the influence of gas-phase corrections on the calculated excess Gibbs energy is small.

ACKNOWLEDGMENT

For the use of its facilities we thank the Computer Center of the University of California, Berkeley, Calif.

Table VII. Predicted Second Virial Coefficients, C_c/Gmol

| Substance | Pitzer-Curl | | | McGlashan | | |
|--------------------|-------------|-------|-------|-----------|-------|-------|
| | 10°C | 30°C | 50°C | 10°C | 30°C | 50°C |
| Benzene | -1794 | -1456 | -1219 | -1528 | -1267 | -1070 |
| Toluene | -2959 | -2332 | -1910 | -2919 | -2360 | -1949 |
| Hexene-1 | -2005 | -1652 | -1396 | -2020 | -1658 | -1388 |
| 2-Methyl-pentene-1 | -1888 | -1576 | -1346 | -2113 | -1731 | -1447 |
| 4-Methyl-pentene-1 | -1760 | -1462 | -1242 | -1895 | -1560 | -1308 |
| Octene-1 | -4435 | -3496 | -2862 | -4951 | -3936 | -3199 |

Table VIII. Predicted Cross Second Virial Coefficients and $\Delta = 2B_{12} - B_{11} - B_{22}$, C_c/Gmol

| System | $T, ^\circ\text{C}$ | Pitzer-Curl | | McGlashan | |
|---------------------------|---------------------|-------------|----------|-----------|----------|
| | | B_{12} | Δ | B_{12} | Δ |
| Benzene-hexene-1 | 10 | -1906 | -13 | -1789 | -30 |
| | 30 | -1559 | -11 | -1474 | -22 |
| | 50 | -1312 | -10 | -1238 | -17 |
| Benzene-2-methylpentene-1 | 10 | -1839 | +4.4 | -1829 | -16 |
| | 30 | -1516 | +0.5 | -1505 | -12 |
| | 50 | -1283 | -1.5 | -1263 | -9.3 |
| Benzene-4-methylpentene-1 | 10 | -1777 | -0.3 | -1733 | -44 |
| | 30 | -1461 | -4.9 | -1430 | -33 |
| | 50 | -1234 | -7.1 | -1202 | -26 |
| Benzene-octene-1 | 10 | -2869 | 490 | -2851 | 777 |
| | 30 | -2295 | 363 | -2306 | 591 |
| | 50 | -1900 | 282 | -1905 | 459 |
| Toluene-hexene-1 | 10 | -2406 | 151 | -2422 | 95 |
| | 30 | -1946 | 92 | -1973 | 72 |
| | 50 | -1624 | 58 | -1641 | 55 |

Table IX. Excess Gibbs Energy of System Benzene-Hexene-1 at 30°C Calculated with Redlich-Kister Three-Parameter Equation I

I. Without vapor-phase corrections. II. With vapor-phase corrections estimated from Pitzer-Curl correlation

| Aromatic mole fraction in liquid | $g^E, \text{cal/gmol}$ | |
|----------------------------------|------------------------|-------|
| | I | II |
| 0.162 | 31.51 | 33.21 |
| 0.261 | 42.55 | 44.50 |
| 0.410 | 52.00 | 53.80 |
| 0.474 | 54.07 | 55.72 |
| 0.597 | 54.81 | 56.16 |
| 0.758 | 47.07 | 48.06 |
| 0.858 | 34.45 | 35.17 |
| 0.931 | 19.65 | 20.07 |

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PVT Properties of Liquid *n*-Octane

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The PVT properties of liquid *n*-octane are presented for six isotherms: -15.00, 5.00, 25.00, 45.00, 65.00, and 85.00°C. The pressure ranged from atmospheric to near freezing at each temperature. The accuracy is estimated at $\pm 0.0006 \text{ cm}^3/\text{cm}^3$. The data were fitted to the Tait equation of state at each temperature. The data were also used to obtain the Tait parameters *L* and *J* as functions of temperature. The error introduced by the temperature fitting averaged 0.041%. The worst error introduced was $0.0017 \text{ cm}^3/\text{cm}^3$.

The PVT data for liquid *n*-octane, as reported in the literature, are inconsistent. Furthermore, the more accurate data do not extend over a large enough range of pressure and temperature to allow the differentiation necessary to calculate accurately thermal properties.

Previous data taken in this laboratory on C₁₀ to C₁₆ normal alkanes showed the slyphon-bellows technique sufficiently accurate to be used for calculating properties requiring two differentiations of the data (14). In this work, *n*-octane is examined from -15° to 85°C at pressures from atmospheric to near freezing.

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EXPERIMENTAL

Apparatus. The operation of the PVT cell can be described with the aid of Figure 1. The two main components of the PVT cell are the bellows, marked *B* on the drawing, and the slide wire, *S*. The slide wire is a section of Karma wire approximately 1 inch in length and 0.010 inch in diameter. Karma is a trademark of the Driver-Harris Co., Harrison, N.J., and is an alloy of nickel, chromium, and aluminum. Karma wire was used as the slide wire because of its low temperature coefficient of resistivity ($0 \pm 10 \text{ ppm}/^\circ\text{C}$), its precision drawn diameter, and its highly uniform linear conductivity (experimentally determined as