must exist as a complex with solvent molecules in DMSO solutions.

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Thermodynamic Properties of Binary Liquid Mixtures Containing Aromatic and Saturated Hydrocarbons

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Total vapor pressure data were obtained for nine binary systems in the temperature range 10–80°C. These data were reduced to obtain excess Gibbs energies.

The properties of liquid hydrocarbon mixtures have been studied by many investigators. Mixtures of saturated hydrocarbons show little deviation from ideal behavior, but solutions of saturated hydrocarbons with aromatics show appreciable nonideality; they often contain azeotropes.

Vapor-liquid equilibrium data are plentiful for mixtures of aromatics with saturated hydrocarbons; however, few of these data are for mixtures of aromatics with branched, saturated hydrocarbons or for mixtures with aromatics containing more than seven carbon atoms. For rational design of distillation equipment and for a fundamental understanding of the effect of molecular structure on thermodynamic properties, we require vapor-liquid equilibrium data for mixtures of aromatics with branched paraffins as well as for mixtures with aromatic molecules containing eight or nine carbon atoms.

In this work we report new vapor-liquid equilibrium data for nine binary systems: 2,2-dimethylbutane–benzene; 2,3-dimethylbutane–benzene; 2-methylpentane–benzene; 3-methylhexane–benzene; 3-methylpentane–toluene; methylcyclohexane–ethylbenzene; *n*-heptane–isopropylbenzene; 2,2,4-trimethylpentane–ethylbenzene; and 3-methylhexane–*n*-propylbenzene. The data are reduced to yield thermodynamic excess functions.

EXPERIMENTAL

Total vapor pressures were measured at constant temperature. A schematic diagram of the apparatus is shown in Figure 1; a detailed description of the apparatus is given by Hermsen (*4*), and modifications are described by Harris (*3*). Advantages and disadvantages of a constant-temperature apparatus are discussed by Scatchard (*8*).

The components used were of the highest purity commercially available. Benzene, toluene, *n*-heptane, 2,2,4-trimethylpentane, and methylcyclohexane from Matheson, Coleman and Bell were more than 99.9% pure. Ethylbenzene, isopropylbenzene, 2-methylpentane, and 3-methylpentane from Phillips Petroleum Co. were also more than 99.9% pure. These hydrocarbons were dried over Linde molecular sieves and used without further purification. 2,2-Dimethylbutane, 2,3-dimethylbutane, and 3-methylhexane from Matheson, Coleman and Bell, along with *n*-propylbenzene from Aldrich Chemical Co. were better than 97% pure. They were further purified by distilling at high reflux in a 10-plate Oldershaw column; the beginning and end fractions were eliminated. All components used showed negligible impurities when analyzed by gas-solid chromatography. This analysis indicates that the impurities probably consist of isomers of the main constituent. Such isomers have a negligible effect on the results reported here.

The components were sealed in separate vacuum stills for degassing. In the measurement of vapor pressures, the prob-

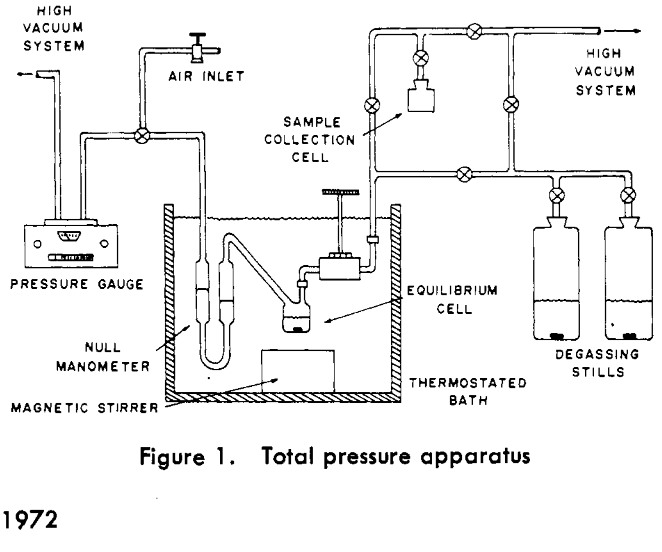

Figure 1. Total pressure apparatus

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Table I. Experimental Vapor-Pressure Data (Pressures are given in mm Hg at 0°C)

x_1	10°C	30°C	50°C
2-Methylpentane(1)–Benzene(2)			
0.000	45.57	118.78	271.45
0.065	58.53	145.69	316.68
0.105	64.80	158.93	341.65
0.325	86.15	204.65	426.32
0.585	98.07	231.22	480.11
0.779	103.77	245.07	513.70
0.880	106.65	250.55	528.97
1.000	109.43	259.44	542.19
2,2-Dimethylbutane(1)–Benzene(2)			
0.000	45.57	118.78	271.45
0.070	74.83	174.60	364.70
0.187	98.23	222.34	459.31
0.301	113.69	254.12	518.28
0.460	129.58	289.73	588.40
0.732	152.87	339.33	678.21
0.902	167.59	367.70	724.63
1.000	172.67	385.69	767.07
2,3-Dimethylbutane(1)–Benzene(2)			
0.000	45.57	118.78	271.45
0.014	50.02	126.05	281.13
0.058	58.82	146.93	319.55
0.155	73.48	176.42	373.54
0.230	82.59	193.85	407.00
0.380	95.11	221.34	460.15
0.515	103.41	239.31	492.81
0.685	111.43	257.78	531.07
0.825	117.21	270.85	558.70
1.000	123.50	285.88	587.13
3-Methylhexane(1)–Benzene(2)			
0.000	45.57	118.78	271.45
0.064	45.76	121.08	273.81
0.139	47.08	121.65	275.38
0.327	46.80	119.55	267.85
0.434	45.76	117.48	263.68
0.565	43.60	111.68	250.78
0.704	41.16	105.09	236.82
0.848	35.51	92.97	211.95
0.855	33.21	91.92	208.86
1.000	28.67	77.95	182.63
3-Methylpentane(1)–Toluene(2)			
0.000	12.48	36.61	92.15
0.069	22.98	59.53	131.57
0.145	32.45	18.62	174.71
0.245	43.86	106.21	229.70
0.370	55.21	132.09	279.55
0.524	65.70	155.14	335.32
0.623	71.89	170.07	367.24
0.713	77.49	185.21	395.11
0.805	83.61	200.56	424.94
0.845	86.20	207.20	437.68
1.000	97.55	233.06	490.78
Methylcyclohexane(1)–Ethylbenzene(2)			
x_1	40°C	60°C	80°C
0.000	21.47	55.48	125.74
0.092	29.50	71.58	155.31
0.137	34.08	80.74	170.86
0.271	45.29	104.29	216.47
0.312	48.47	111.44	229.74
0.355	51.98	118.11	243.11
0.492	60.49	138.09	282.03
0.519	62.89	141.92	288.47
0.586	67.05	150.31	305.22
0.676	72.01	161.30	327.09
0.842	81.47	181.52	365.56
1.000	91.62	202.84	404.50
n-Heptane(1)–Isopropylbenzene(2)			
0.000	10.98	30.32	72.49
0.138	26.55	63.45	136.33
0.297	40.96	95.16	198.18
0.428	51.35	118.08	244.24
0.582	62.29	142.97	294.06
0.716	71.78	164.56	336.53
0.780	75.71	174.05	356.39
0.913	85.20	195.38	398.62
1.000	92.50	210.52	427.30
2,2,4-Trimethylpentane(1)–Ethylbenzene(2)			
0.000	21.50	55.49	125.80
0.121	36.25	85.81	181.47
0.194	43.65	101.13	208.93
0.298	52.20	119.21	243.27
0.366	57.64	130.13	264.58
0.406	60.52	136.18	276.07
0.456	63.89	143.57	290.19
0.574	71.49	159.45	322.04
0.661	76.64	171.18	343.95
0.738	81.28	180.69	363.30
0.824	86.50	191.91	383.87
1.000	97.22	214.52	425.91
3-Methylhexane(1)–*n*-Propylbenzene(2)			
0.000	8.24	23.42	57.25
0.126	28.94	66.53	138.08
0.174	35.78	80.22	163.54
0.278	47.86	107.03	215.41
0.364	57.93	127.68	255.65
0.493	71.40	157.68	313.54
0.609	82.93	182.88	363.61
0.701	91.28	201.91	401.58
0.830	103.46	228.83	455.23
1.000	121.16	266.40	528.37

lem of degassing the components is the most serious; unless the pure components are thoroughly degassed, vapor pressures are too high. To remove most of the dissolved air, the pure components were vigorously agitated by a magnetic stirrer while the degassing stills were open to a vacuum system. Upon repeating this flashing operation several times, the hydrocarbons were nearly completely degassed. However, to avoid excessive loss of material, this technique was not used for complete degassing of the components. Instead, residual air was removed by freezing the components with liquid nitrogen and opening the stills to a vacuum system. Repeating this freezing operation several times gave thoroughly degassed components.

The degassed components were transferred to the equilibrium cell by distilling from the degassing stills and condensing in the equilibrium cell with liquid nitrogen.

The cell was gradually warmed and thermostated. The small null manometer was kept approximately in balance by bleeding air into the reference side of the manometer through a needle valve. The equilibrium cell was magnetically stirred to assure thorough mixing of the components and uniform temperature. Equilibrium was attained in about 40 min. Pressure was measured with a Texas Instruments fused-quartz pressure gauge, periodically standardized using a mercury manometer. The small null manometer was read using a Wild-Heerbrugg cathetometer.

Vapor-pressure measurements were made at progressively higher temperatures. After measurement at the highest temperature, the sample was transferred from the equilibrium cell by vaporizing it completely into a previously evacuated collection cell. A vacuum gauge indicated when transfer was complete. The index of refraction of the sample was measured by a Bausch and Lomb refractometer thermostated at 25°C. For calibration, samples of known composition were prepared and their refractive indices measured. Because the sample composition corresponds to the total composition of the liquid and vapor, a correction must be applied to calculate the true liquid composition. The true liquid composition can be calculated readily from the total composition, pressure, temperature, volume of the cell, and weight of the mixture. A one-parameter Margules expression is assumed for the liquid-phase activity coefficients; by trial and error that liquid-phase composition is found which satisfies both the equations of equilibrium and the mass balances. Since the experimental pressures were low and the vapor volume was small, total compositions were virtually equal to liquid-phase compositions.

Vapor pressures were measured to within ±0.10 mm Hg. The temperature of the bath was thermostated to ±0.01°C; this uncertainty in temperature causes a maximum error of ±0.10% in the vapor pressure. The mixtures used for the index-of-refraction calibration were accurate to within ±0.001 mole fraction. The index of refraction could be measured to within ±0.0001 at 25°C. An error of less than ±0.002 in mole fraction was introduced by interpolating on the calibration curve to find sample compositions. These experimental errors are small enough to ensure that the experimental vapor pressures are accurate to ±0.50% or better at each temperature. Experimental results for the nine binary systems studied are given in Table I.

DATA REDUCTION

Vapor-liquid equilibrium data for mixtures of aromatic and saturated hydrocarbons were reduced to calculate the excess Gibbs energy by a method described previously (*6*, *7*). For a binary mixture, the molar excess Gibbs energy g^E is a function of the mole numbers n_1 and n_2:

$$(n_1 + n_2)\, g^E = \mathfrak{f}(A, B, C \ldots n_1, n_2) \tag{1}$$

where $A, B, C \ldots$ are adjustable parameters which depend upon temperature but not composition. The form of the function $\mathfrak{f}$ is arbitrary, except that it must satisfy the boundary conditions: $\mathfrak{f} = 0$ when $n_1 = 0$ and $n_2 = 0$. Activity coefficients can be found from Equation 1 using the exact relation

$$RT \ln \gamma_i = [\partial(n_1 + n_2)\, g^E / \partial n_i]_{T,P,n_{j \neq i}} \tag{2}$$

where R is the gas constant and T is the absolute temperature. With assumed values of the parameters A, B, $C \ldots$, the total pressure of the binary mixture can be calculated by

$$P = \frac{x_1 \gamma_1 f_1^0}{\phi_1} + \frac{x_2 \gamma_2 f_2^0}{\phi_2} \tag{3}$$

where x is the liquid-phase mole fraction, ϕ is the vapor-phase fugacity coefficient, and f^0 is the fugacity of pure component i in the liquid phase at system temperature and pressure. Fugacity coefficients were calculated using second virial coefficients as described previously (*7*). The fugacity of pure liquid i is given by the product of the saturation (vapor) pressure P_i^S, the fugacity coefficient φ_i^S at P_i^S, and the Poynting correction:

$$f_i^0 = P_i^S \phi_i^S \exp\{v_i(P - P_i^S)/RT\} \tag{4}$$

where v_i is the liquid molar volume of pure i. Fugacity coefficients φ_i^S were estimated from Lyckman's correlation (*5*).

Table II. Comparison of Equations for Representing Excess Gibbs Energy of System 2-Methylpentane–Benzene at 30°C

Equation	% Std dev in pressure[a]
Redlich-Kister (2-parameter) $\frac{g^E}{RT} = x_1 x_2 [A + B(x_1 - x_2)]$	0.88
Wilson (2-parameter) $\frac{g^E}{RT} = x_1 \ln (x_1 + \Lambda_{12} x_2) - x_2 \ln (x_2 + \Lambda_{21} x_1)$	0.67
Redlich-Kister (3-parameter) $\frac{g^E}{RT} = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2]$	0.54
Renon NRTL (3-parameter) $\frac{g^E}{RT} = x_1 x_2 \left[\frac{\tau_{21} \exp(-\alpha\tau_{21})}{x_1 + x_2 \exp(-\alpha\tau_{21})} + \frac{\tau_{12} \exp(-\alpha\tau_{12})}{x_2 + x_1 \exp(-\alpha\tau_{12})}\right]$	0.46

[a] % std dev $= 100 \sqrt{\sum_N \left(\frac{P_{\text{exp}} - P_{\text{cal}}}{P_{\text{exp}}}\right)^2 / N}$ where N is the number of experimental points.

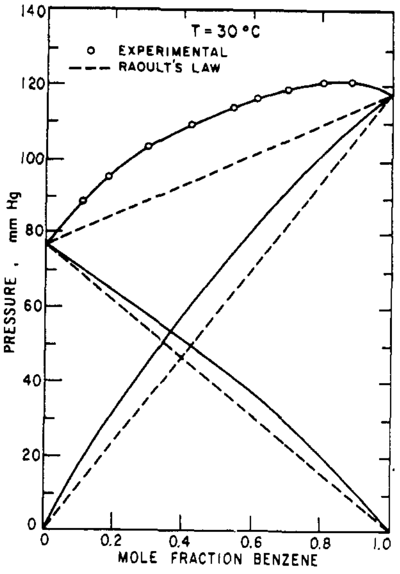

Figure 2. Total and partial pressures for 3-methylhexane–benzene system

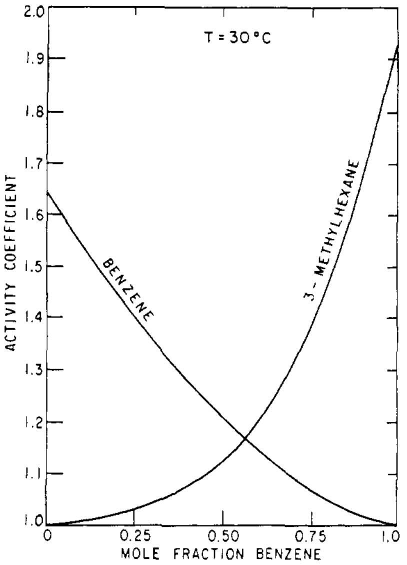

Figure 3. *Activity coefficients for 3-methylhexane–benzene system*

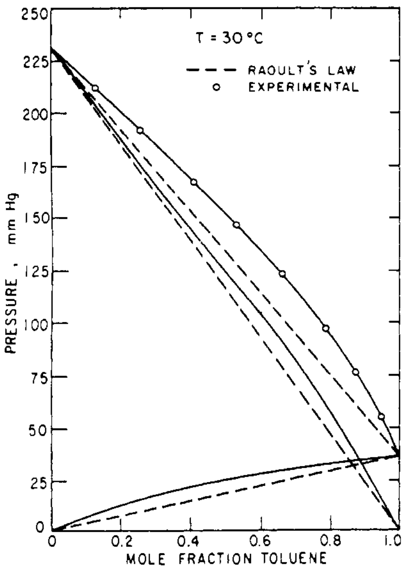

Figure 4. Total and partial pressures for 3-methylpentane–toluene system

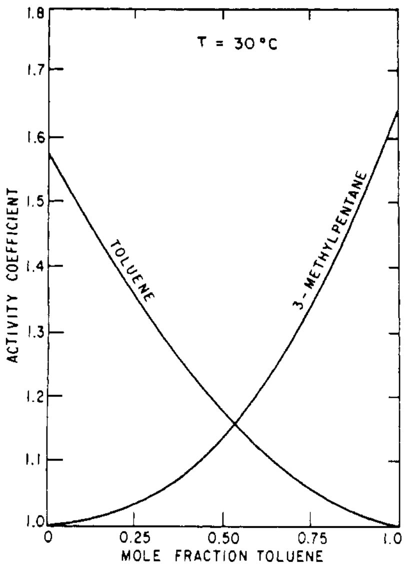

Figure 5. Activity coefficients for 3-methylpentane–toluene system

For a particular function f, calculated and observed pressures were compared; the sum of the squared deviations in pressure was calculated, and a nonlinear regression on the parameters A, B, C . . . was carried out to minimize the sum of the squared deviations.

RESULTS

Experimental vapor pressures were fitted using four equations for the excess Gibbs energy; these equations discussed in ref. 7, are given in Table II. Table II also shows a comparison of the fit obtained for the system 2-methylpentane–benzene. The three-parameter Redlich-Kister equation and the Renon NRTL equation give a significantly better fit than the two-parameter Redlich-Kister equation. Although the Wilson equation contains only two adjustable parameters, it gives almost as good a fit as the three-parameter equations. Deviations between experimental and calculated pressures were approximately equal to the estimated experimental errors. Redlich-Kister parameters and Wilson parameters for the nine systems studied have been deposited with ACS Primary Publications Microfilm Depository Service.

Figure 2 shows the total pressure as a function of liquid composition for the 3-methylhexane–benzene system at 30°C; this system is moderately nonideal and contains an azeotrope. Figure 3 shows the activity coefficients for this system.

Figure 4 shows the total pressure-composition curve for the 3-methylpentane–toluene system at 30°C, and Figure 5 shows the activity coefficients. This system is more ideal than similar benzene-saturated hydrocarbon systems.

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