Vapor-Liquid Equilibria at 25° C in the Binary Mixtures Formed by Hexane, Benzene, and Ethanol

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Total vapor pressures for the binary systems *n*-hexane–benzene, benzene-ethanol, and *n*-hexane–ethanol were measured at 25° C using a static vapor pressure apparatus of simple design. Excess Gibbs energies were calculated from the data by the rigorous procedure of Mixon, Gumowski, and Carpenter; the results were combined with literature heat-of-mixing data to arrive at values of G^E, H^E, and S^E for each system. The data were also compared with the van Laar, Redlich-Kister, and Wilson expressions for the excess Gibbs energy.

ANY satisfactory liquid solution model should adequately represent both the excess Gibbs energy and excess enthalpy (and thus the excess entropy) of mixtures. These excess properties are conveniently determined from experimental vapor-liquid equilibria and heat-of-mixing data. However, surprisingly few systems have been subjected to precise measurements of both vapor-liquid equilibria and heats-of-mixing at the same isothermal conditions. In the present study, a simple apparatus was designed to facilitate measurement of total solution vapor pressures to provide excess Gibbs energy data on systems where excess enthalpies are currently available. The static vapor pressure technique was selected to eliminate the tedious and potentially inaccurate vapor phase sampling and analysis.

EXPERIMENTAL

Apparatus. Complete details of the experimental work are given elsewhere (*10*). Briefly, the equilibrium cell was constructed of borosilicate glass tubing and a high-vacuum, three-way stopcock (Westglas Corp., Catalog No. W-1846). A schematic drawing of the cell is shown in Figure 1. Over-all height of the cell is approximately 30 cm. The stopcock, *A*, permitted communication to be established between the side arms, *B* and *C*, side arm *B*, and the cell, *D*, or *B*, *C*, and *D*. Pressures were measured with an absolute pressure transducer (Consolidated Electrodynamics, Type 4-313, 0 to 20 psia) connected to side arm *B* by a lubricated glass ball joint. The transducer was periodically calibrated against a fused quartz precision pressure gage (Texas Instruments, Model 141A). Accuracy of calibration is estimated as 0.05 mm of Hg. In operation, the cell was submerged in a water bath to a level just below side arm *C*. Bath temperature was measured by a mercury-in-glass thermometer having 0.01° C divisions; the thermometer was calibrated at 25° C against a platinum resistance thermometer which had been calibrated by the National Bureau of Standards. Accuracy of calibration is estimated as 0.02° C.

Procedure. Each experimental run began with gravimetric preparation of a liquid mixture of the desired composition. Approximately 40 cc of the mixture was transferred to the equilibrium cell. The mixture was degassed within the cell as follows. First, the mixture was boiled under total reflux (maintained by use of the condenser, *F*) at 200 to 300 mm of Hg pressure for approximately one hour. The coolant flow to the condenser was then reduced and the condensate level was allowed to rise in the condenser until it reached the base of the open stopcock plug, at which time the stopcock was closed. The mixture was then frozen in place and the vapor space evacuated through side arm *C*. The stopcock was reclosed and the mixture was thawed. Satisfactory degassing was judged by absence of bubble formation during thawing. Tests showed no detectable change in mixture composition during degassing operations. Vaporization of liquid to fill the vapor space in the cell also produced negligible changes in liquid compositions.

After degassing, the cell was lowered into a water bath controlled at a temperature of 25° ± 0.015° C. Sufficient time was allowed for attainment of thermal equilibrium, during which time the mixture was stirred by a metal-in-glass spin bar, *G*. After equilibrium was established, the cell was opened to the transducer through side arm *B* (previously evacuated), stirring was stopped, and pressure was monitored until successive readings became constant.

Materials. The *n*-hexane and benzene used were Phillips Petroleum Co. research grade materials with specified minimum purities of 99.9 mole %. The ethanol was reagent

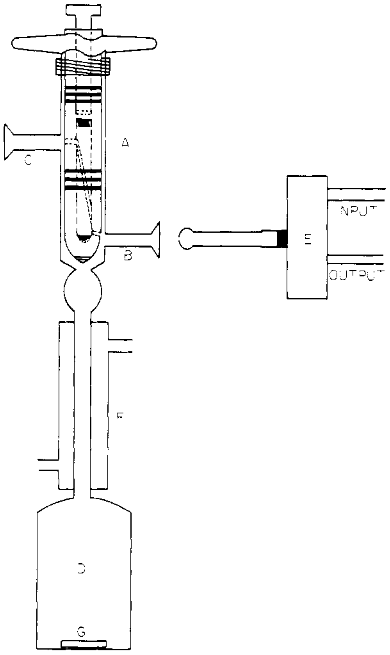

Figure 1. Vapor pressure apparatus

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grade supplied by the U.S. Industrial Chemical Co. All materials were used without further purification.

RESULTS

Experimental data on the pure component vapor pressures are given in Table I and compared with literature values. Agreement is good for benzene and ethanol, but for hexane the difference, 1.55 mm of Hg, is well outside the experimental uncertainty. Hanson and Van Winkle (*4*) recently reported similar disagreement with literature data on hexane at 60° C, where their measurements were 1.2 mm of Hg above the literature value. For other components they found excellent agreement. Based on the reproducibility of the present measurements and agreement with literature data on benzene and ethanol, the pure component and mixture vapor pressures are estimated to be accurate to within ±0.3 mm of Hg. Maximum uncertainties in liquid mole fractions are estimated as ±0.001 and calculated vapor mole fractions as ±0.002.

Table I. Pure Component Vapor Pressures at 25° C

Component	Vapor Pressure, Mm Hg Exptl.	Vapor Pressure, Mm Hg Lit.
n-Hexane	152.8_5 (2,0.15)	151.30 (*11*)
Benzene	95.2_5 (1,-)	95.10 (*11*)
Ethanol	59.0_5 (6,0.23)[a]	59.02 (*11*)

[a] Number of replicate measurements, average absolute deviation from mean.

Table II. Vapor Pressure Data at 25° C

(1) (2) *n*-Hexane–Benzene x_1	 π, mm Hg	(1) (2) Benzene-Ethanol x_1	 π, mm Hg	(1) (2) *n*-Hexane–Ethanol x_1	 π, mm Hg
0.000	95.2_5	0.000	59.0_5	0.000	59.0_5
0.108_5	116.8_5	0.101_5	89.5	0.100_5	145.1_5
0.205_5	126.8_5	0.200	106.3_5	0.205	173.4
0.299	134.6_5	0.299_5	115.6	0.292	182.2
0.381	139.7_5	0.410	120.9	0.403	188.1_5
0.502	114.5_5	0.498	123.3_5	0.490	188.8_5
0.549	147.4_5	0.596	124.4_5	0.603	189.8_5
0.700_5	150.5	0.692	124.7_5	0.736	190.7_5
0.799	152.9	0.807	124.3	0.894_5	189.5_5
0.897_5	154.2	0.899	121.6_5	0.945_5	187.6_5
1.000	152.8_5	1.000	95.2_5	0.973_5	183.8_5
				1.000	152.8_5

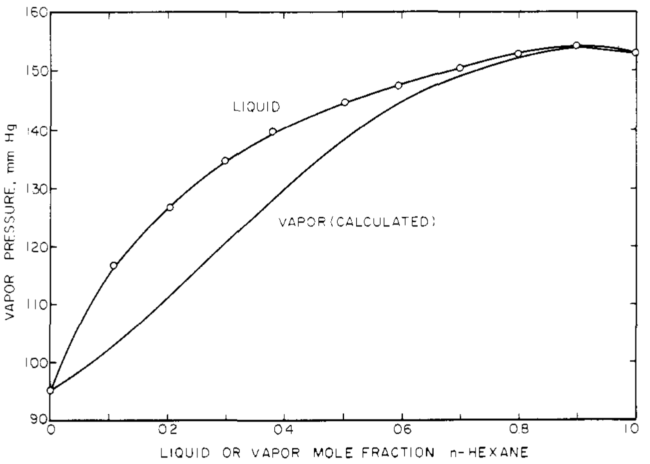

Figure 2. Vapor pressure at 25° C for system *n*-hexane–benzene

The solution vapor pressure data from this study are given in Table II and Figures 2, 3, and 4. Calculated vapor compositions, discussed below, are also shown in the figures.

DATA REDUCTION

The vapor pressures were related to the excess Gibbs energies by the following equations.

$$\pi = x_1\gamma_1^L p_1^*/F_1 + x_2\gamma_2^L p_2^*/F_2 \tag{1}$$

where

$$RT \ln \gamma_1^L = \{\partial(n_T G^E)/\partial n_1\}_{T,\,p,\,n_2} \tag{2}$$

$$F_1 = \phi_1^V/\nu_1^* \exp\left[V_1^L(\pi - p_1^*)/RT\right] \tag{3}$$

with similar expressions for γ_2^L and F_2. The values of ϕ_i^V and ν_i^* were evaluated from the virial equation of state truncated after the second virial coefficient term. Pure and interaction virial coefficients were estimated from the correlation of O'Connell and Prausnitz (*8*).

Equations 1 through 3 were utilized in an iterative numerical procedure, described by Mixon, Gumowski, and Carpenter (*7*), to establish the $G^E - x_1$ relation from the $\pi - x_1$ data. The procedure consists of iterative improvements in an initially assumed tabular $G^E - x_1$ relation until a

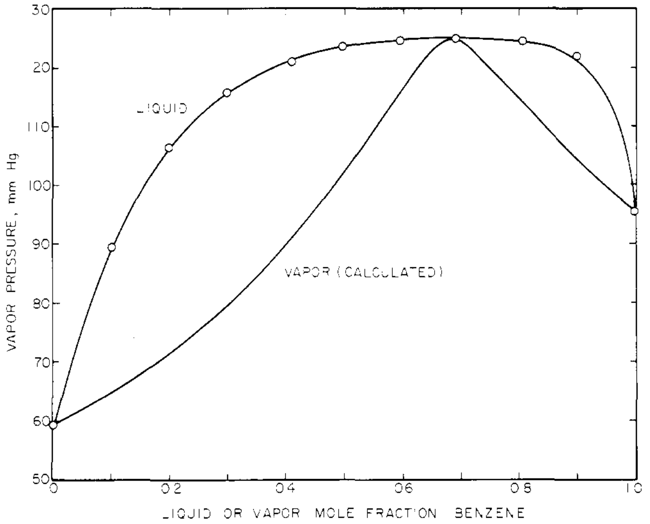

Figure 3. Vapor pressure at 25° C for system benzene-ethanol

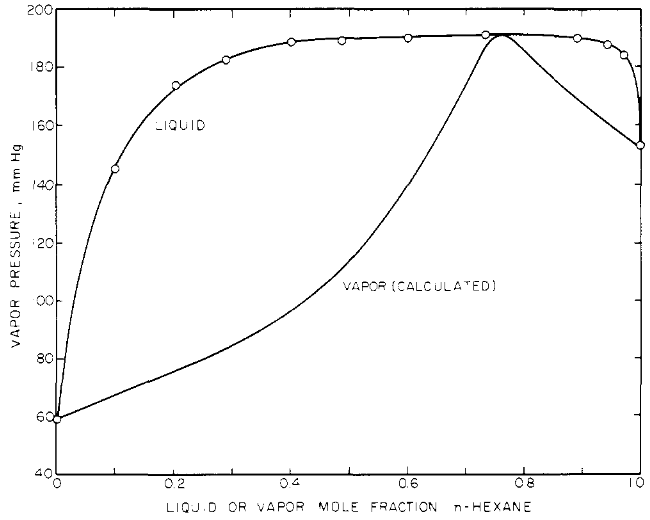

Figure 4. Vapor pressure at 25° C for system *n*-hexane–ethanol

precise fit to the tabular (smoothed) $\pi - x_1$ data is obtained. Details of the calculations are given elsewhere (*10*). The particular merit of the above procedure is that the resultant excess Gibbs energy values are independent of any assumed analytical model for the excess Gibbs energy, such as results from the usual procedure (*1*) for establishing the $G^E - x_1$ relation from vapor pressure data. The $G^E - x_1$ results from the Mixon, Gumowski, and Carpenter method can be made to reproduce the $\pi - x_1$ data to any desired degree of accuracy. In the present work, the agreement was to about 0.02 mm of Hg standard error in π.

From the final $G^E - x_1$ values, vapor compositions were calculated from the equation

$$y_1 = x_1\gamma_1^L p_1^* / F_1\pi \qquad (4)$$

Complete results of the calculations are shown in Table III and Figures 5, 6, and 7. Also included are literature H^E values and TS^E values calculated as

$$TS^E = H^E - G^E \qquad (5)$$

Several analytical expressions for the excess Gibbs energy were also fitted to the present data. The equations employed are given below.

VAN LAAR EQUATION (*12*)

$$G^E/RT = x_1x_2A_{12}A_{21}/(x_1A_{12} + x_2A_{21}) \qquad (6)$$

REDLICH-KISTER EQUATION (*9*)

$$G^E/RT = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2 + D(x_1 - x_2)^3 + \ldots] \qquad (7)$$

WILSON EQUATION (*13*)

$$G^E/RT = -x_1\ln(x_1 + \Lambda_{12}x_2) - x_2\ln(x_2 + \Lambda_{21}x_1) \qquad (8)$$

The method for applying these equations to the data has been described by Barker (*1*). In essence, the param-

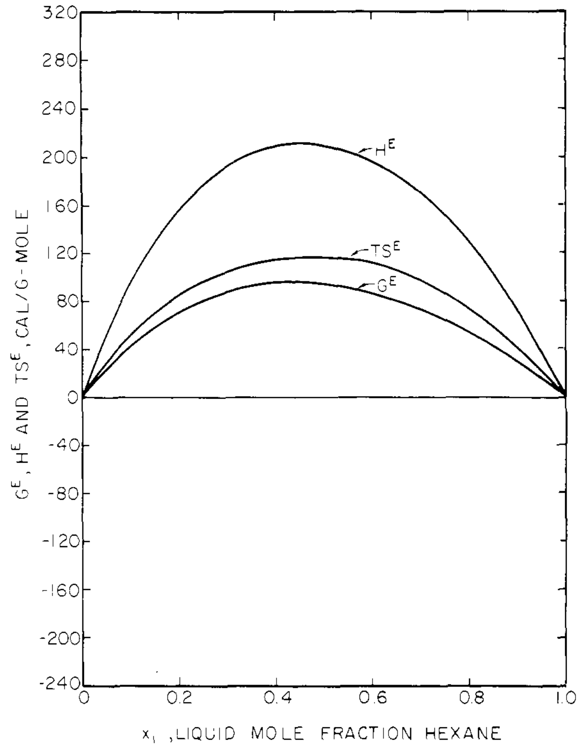

Figure 5. Excess thermodynamic properties at 25° C for system *n*-hexane–benzene

Table III. Vapor-Liquid Equilibrium Data and Excess Mixing Properties at 25° C

x_1	π, Mm Hg	y_1	γ_1	γ_2	G^E, Cal/G-Mole	H^E (*6*), Cal/G-Mole	TS^E, Cal/G-Mole
			SYSTEM *n*-HEXANE–BENZENE[a]				
0.1	115.4	0.242	1.834	1.019	45.84	96.0	50.2
0.2	126.4	0.363	1.505	1.053	73.05	160.0	87.0
0.3	134.5	0.456	1.338	1.095	89.23	194.0	105.8
0.4	140.4	0.529	1.215	1.153	96.75	211.0	114.3
0.5	144.5	0.592	1.120	1.232	95.38	211.0	115.6
0.6	147.7	0.661	1.064	1.309	85.78	198.0	112.2
0.7	150.6	0.744	1.046	1.345	71.33	171.0	99.4
0.8	153.0	0.820	1.019	1.429	51.13	128.0	73.3
0.9	154.3	0.904	1.013	1.550	32.76	72.0	39.3
			SYSTEM BENZENE-ETHANOL[b]				
0.1	89.5	0.397	3.750	1.007	80.50	43.0	−37.5
0.2	106.5	0.530	2.970	1.050	149.41	82.0	−67.4
0.3	115.7	0.594	2.407	1.126	201.78	120.0	−81.8
0.4	120.8	0.632	2.004	1.243	237.96	157.0	−80.9
0.5	123.5	0.658	1.704	1.419	257.29	188.0	−69.3
0.6	124.4	0.672	1.462	1.712	257.94	209.0	−48.9
0.7	124.9	0.688	1.287	2.183	239.35	216.0	−23.3
0.8	124.5	0.700	1.143	3.140	195.37	203.0	7.2
0.9	121.2	0.740	1.045	5.303	120.11	156.0	35.0
			SYSTEM *n*-HEXANE–ETHANOL[a]				
0.1	145.2	0.620	5.919	1.033	120.64	46.0	−74.6
0.2	172.1	0.694	3.910	1.110	207.31	79.0	−128.3
0.3	182.8	0.721	2.872	1.229	268.30	103.0	−165.3
0.4	187.5	0.734	2.248	1.401	306.69	120.5	−186.2
0.5	189.1	0.739	1.827	1.661	323.29	133.0	−190.3
0.6	190.0	0.744	1.539	2.051	317.93	138.0	−179.9
0.7	190.4	0.749	1.330	2.685	288.92	136.0	−152.9
0.8	190.4	0.758	1.178	3.883	234.46	126.0	−108.5
0.9	189.4	0.776	1.067	7.138	148.54	102.0	−46.5

[a] Component 1, *n*-Hexane. [b] Component 1, benzene.

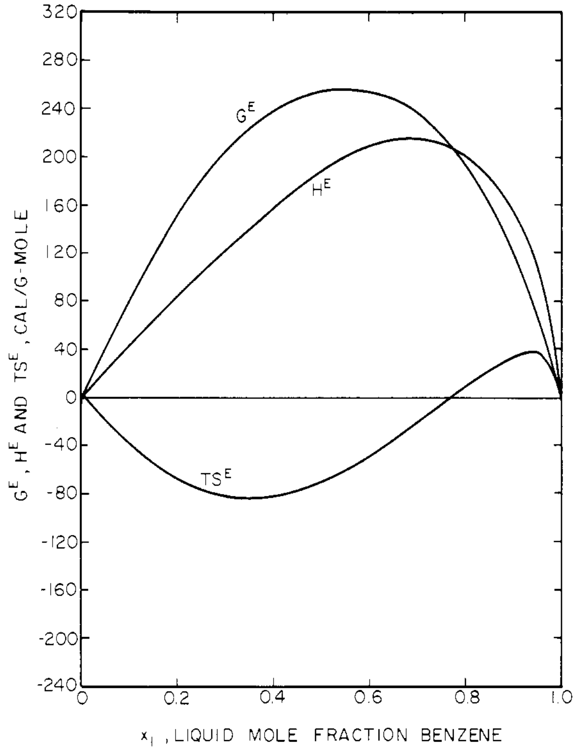

Figure 6. Excess thermodynamic properties at 25° C for system benzene-ethanol

eters in the above equations are established by regression to provide least-squares deviations between calculated and experimental pressures. Table IV shows the accuracy with which these equations are able to represent the experimental data. Parameter values for the Wilson and four-parameter Redlich-Kister equations are reported in Tables V and VI.

DISCUSSION

No other vapor-liquid equilibria data at 25° C have been published for the systems of this study, but several data sets are available at higher temperatures. These higher temperature data, the present data, and published heat-of-mixing data provide an opportunity for tests of mutual consistency among the data. The Gibbs-Duhem equation may be integrated at constant composition to yield

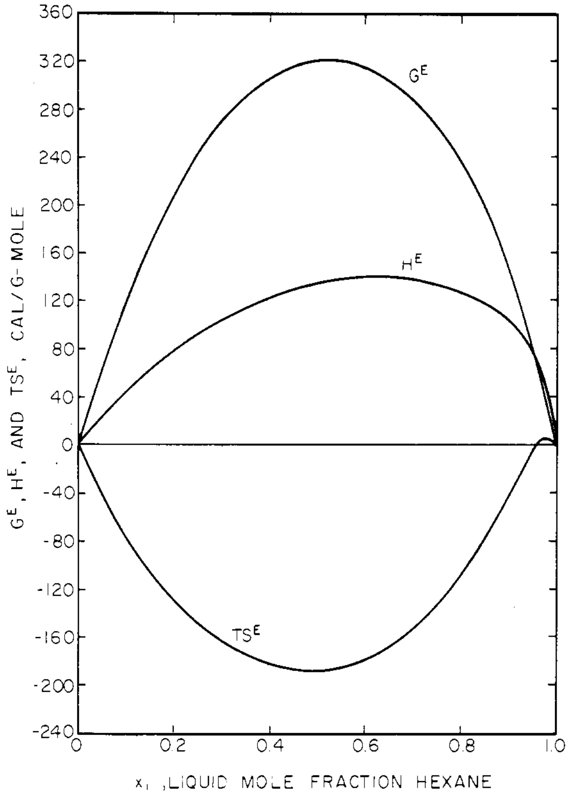

Figure 7. Excess thermodynamic properties at 25° C for system *n*-hexane–ethanol

$$(G^E/T)_{T_2} = (G^E/T)_{298^\circ\text{ K}} - \int_{298^\circ\text{ K}}^{T_2} (H^E/T^2)dT + \int_{\pi_{298^\circ\text{ K}}}^{\pi_{T_2}} (V^E/T)dp \qquad (9)$$

In the present application, the pressure integral has been shown to be entirely negligible (*10*). Data consistency tests were made on several systems by evaluating the right side of Equation 9 from the present data and literature H^E data (generally available at several temperatures between 298° K and T_2). G^E values at T_2 were then converted to total solution vapor pressures and vapor mole fractions. Typical results are shown in Figures 8 and 9 for comparison

Table IV. Comparison of Fit to Experimental Pressures for Analytical Models

Model	(1) (2) *n*-Hexane–Benzene		(1) (2) Benzene-Ethanol		(1) (2) *n*-Hexane–Ethanol	
	Standard error, σ, mm Hg	Max. abs. error, mm Hg	Standard error, σ, mm Hg	Max. abs. error, mm Hg	Standard error, σ, mm Hg	Max. abs. error, mm Hg
van Laar	0.50[a]	0.99[b] (0.897$_5$)[c]	0.95	1.76 (0.899)	7.76	15.65 (0.973$_5$)
Wilson	0.48	0.95 (0.897$_5$)	0.17	0.34 (0.101)	1.56	3.20 (0.973$_5$)
Redlich-Kister						
2-parameter	0.63	1.19 (0.897$_5$)	1.42	2.90 (0.899)	8.36	17.60 (0.973$_5$)
3-parameter	0.43	0.65 (0.381)	0.43	0.75 (0.899)	3.81	9.09 (0.973$_5$)
4-parameter	0.38	0.70 (0.205$_5$)	0.07	0.14 (0.498)	2.36	4.87 (0.973$_5$)

[a] Standard error of estimate $= \left[\sum_{i=1}^{n} (\pi_{\text{exptl.}} - \pi_{\text{calcd.}})_i^2 / n \right]^{1/2}$

[b] Maximum absolute error = maximum value of $[(\pi_{\text{exptl.}} - \pi_{\text{calcd.}})]$. [c] Numbers in parentheses values of x_1 at which maximum error occurs.

Table V. Wilson Parameters for Each System at 25° C

System[a]	$(\lambda_{12} - \lambda_{11})$, Cal/G-Mole	Λ_{12}[b]	$(\lambda_{21} - \lambda_{22})$, Cal/G-Mole	Λ_{21}
Hexane-benzene	384.47	0.3607	148.42	1.1278
Benzene-ethanol	154.89	0.5058	1621.00	0.0987
Hexane-ethanol	354.79	0.2489	2209.77	0.0530

[a] Component 1 is first component listed for each system.

[b] $\Lambda_{ij} = \frac{V_j^L}{V_i^L} \exp - \frac{(\lambda_{ij} - \lambda_{ii})}{RT}$

Table VI. Four-Parameter Redlich-Kister Constants for Each System at 25° C

System	A	B	C	D
Hexane-benzene	0.6403	−0.1871	0.0832	0.0737
Benzene-ethanol	1.7633	0.3548	0.2543	0.1608
Hexane-ethanol	2.1933	0.2083	0.5320	0.4003

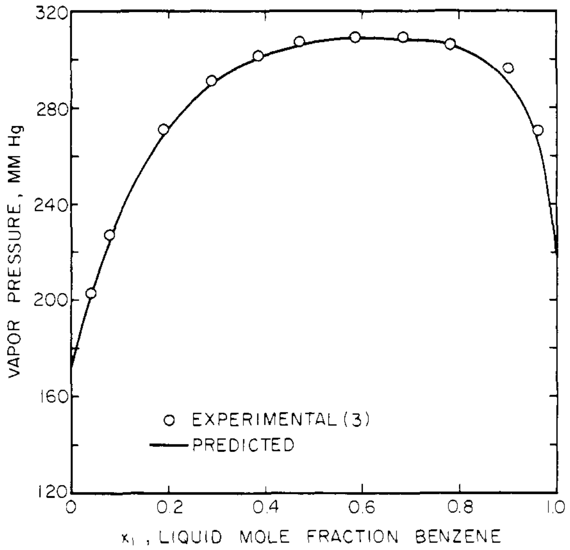

Figure 8. Predicted and experimental vapor pressure at 45° C for system benzene-ethanol

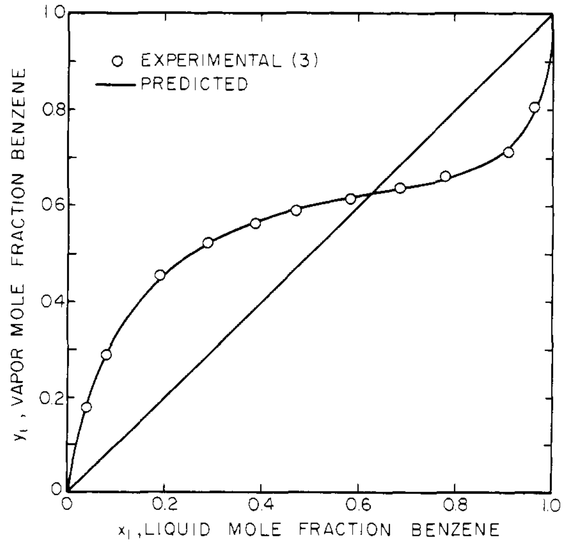

Figure 9. Predicted and experimental vapor composition at 45° C for system benzene-ethanol

with the 45° C benzene-ethanol equilibrium data of Brown and Smith (3), using the heat of mixing data of Brown and Fock (2). The predicted vapor pressures at 45° C differed from the experimental data by an average of 1.5 mm of Hg, and vapor mole fractions differed by 0.003. Similar results were found for other systems tested, calculated pressures at the higher temperatures being in general below the experimental values while vapor mole fractions agreed well.

The ability of the analytical expressions for G^E to fit the experimental pressure data, as shown in Table VI, substantiates results reported by others (*5, 14*); the Wilson equation is the best of the two-parameter equations, often superior to higher order Redlich-Kister expressions.

Figures 2, 3, and 4 show that each of the systems possesses an azeotrope. Azeotrope compositions were estimated as 0.920 mole fraction for hexane-benzene, 0.688 for benzene-ethanol, and 0.755 for hexane-ethanol.

ACKNOWLEDGMENT

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NOMENCLATURE

A, B, C, D = Redlich-Kister constants
A_{ij} = van Laar constant
F = variable defined by Equation 3
G = molal Gibbs free energy, cal/g-mole
H = molal enthalpy, cal/g-mole
n = number of data points
n_i = moles of component i
n_T = total number of moles in a mixture
p = pressure
p^* = pure component vapor pressure, mm Hg
R = Universal gas law constant
S = molal entropy, cal/g-mole ° K
T = absolute temperature, ° K
V = molar volume, cc/g-mole
x = liquid mole fraction
y = vapor mole fraction
γ = activity coefficient
λ = Wilson parameter, cal/g-mole
ν_i^* = fugacity coefficient of pure i at temperature of mixture and pressure p_i^*
π = mixture vapor pressure, mm of Hg
σ = standard error of estimate
ϕ_i^V = vapor phase fugacity coefficient of component i

Superscripts

E = excess thermodynamic property
L = liquid phase
V = vapor phase

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