Vapor-Liquid Equilibria of Binary Systems Containing *n*-Hexane, Cyclohexane, and Benzene at Low Temperatures

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Total vapor pressures of the binary mixtures cyclohexane–benzene, *n*-hexane–cyclohexane, and *n*-hexane–benzene were determined by a static method from 0° to 25°C and correlated by the Antoine equation. Both direct and indirect methods were employed to calculate the vapor compositions and the total vapor pressures. Results from these two methods are in close agreement, with standard deviations of less than 0.006 mole fraction and 0.4 mm Hg, respectively.

Vapor-liquid equilibrium data of hydrocarbon mixtures at low temperatures are useful in the study of oil pollution in a cold environment. They are also of interest to petroleum and related industries. In the literature, considerable work has been published on vapor-liquid equilibria of binary systems containing cyclohexane, *n*-hexane, and benzene (*2, 3, 8, 9, 12, 14–18*). However, data for these systems at temperatures below 25°C are hardly available.

In the present investigation, total vapor pressures for the binary systems mentioned above at temperatures between 0° and 25°C are experimentally determined at constant liquid compositions and correlated by the Antoine equation, from which isothermal *P-x* values are obtained. The equilibrium vapor compositions are computed by both direct and indirect methods. The *P-x-y* values obtained are presented at 0°, 5°, 10°, 15°, 20°, and 25°C for the three binary systems.

Experimental

The experimental apparatus, shown schematically in Figure 1, is essentially the same as that used in a previous study (*8*) except that a precision quartz gage (Texas Instruments) was employed for the total vapor-pressure measurements. The gage was connected with the equilibrium cell by a capillary glass tube and calibrated by measuring the vapor pressure of pure *n*-hexane, cyclohexane, and benzene. The quartz spiral of the gage was thermostated at 44.2 ± 0.1°C.

Preparation of the sample and evacuation of the system followed the procedures previously reported (*8*). After the system was evacuated, Valve 1 was closed and Valve 2 opened. The degassed solution was then distilled into the equilibrium cell. At equilibrium, the temperature and total vapor pressure were recorded. The liquid composition of the solution was determined by measuring its density at 25°C, with pycnometers. Precision of the temperature, pressure, and composition measurements are estimated to be ±0.005°C, ±0.03 mm Hg, and ±0.005 mole fraction, respectively. The composition change of the liquid phase, owing to vaporization in the equilibrium cell, was estimated to be negligible in all the determinations.

Research grade *n*-hexane (99.99 mol % purity), cyclohexane (99.99 mol % purity), and benzene (99.90 mol % purity), supplied by Philips Petroleum Co., were used without further purification. Their refractive indices and densities are given in Table I.

Results and Discussion

The total vapor pressures measured for the three binary systems are listed in Tables II–IV. The Antoine constants obtained for correlating the total vapor pressures at constant compositions are listed in Table 5 (Tables 5 and 7–12 have been deposited with the ACS Microfilm Depository Service). These constants are used to evaluate the isothermal total vapor pressure–liquid composition values, whereas the equilibrium vapor compositions are calculated by both direct and indirect methods as follows:

Indirect method (1). In this investigation, the liquid-phase activity coefficients are represented by means of the Redlich-Kister equation (*13*):

$$\ln \gamma_1 = x_2^2\,[B + C(4x_1 - 1) + D(2x_1 - 1)(6x_1 - 1)] \tag{1A}$$

$$\ln \gamma_2 = x_1^2\,[B + C(4x_1 - 3) + D(2x_1 - 1)(6x_1 - 5)] \tag{1B}$$

At low pressures, the activity coefficient for component *i* in a binary solution is given by the following equation (*19*):

$$\ln \gamma_i = \ln \frac{y_i P}{x_i p_i} + \frac{(\beta_{ii} - V_i)(P - p_i)}{RT} + \frac{P\delta_{12} y_j^2}{RT} \tag{2}$$

where

$$\delta_{12} = 2\beta_{12} - \beta_{11} - \beta_{22} \tag{3}$$

Rearranging Equation 2 gives:

$$P = x_1\gamma_1 p_1 \exp\left[\frac{-(\beta_{11} - V_1)(P - p_1) - P\delta_{12} y_2^2}{RT}\right] + x_2\gamma_2 p_2 \exp\left[\frac{-(\beta_{22} - V_2)(P - p_2) - P\delta_{12} y_1^2}{RT}\right] \tag{4}$$

After substituting Equation 1 into Equation 4, the total vapor pressure is a nonlinear function of the liquid composition and the coefficients *B*, *C*, and *D*. These coefficients are evaluated by means of the nonlinear regression technique proposed by Ho et al. (*7*) and are listed in Table VI. The second virial coefficients, β_{11} and β_{22}, were calculated according to the equation of Pitzer and Curl (*11*), whereas the cross coefficient β_{12} was determined by the method of O'Connell and Prausnitz (*10*).

In the first approximation, the term $(p\delta_{12} y_j^2/RT)$ in Equation 2 was neglected. The *y* values obtained from this approximation are used in the evaluation of this term in the second approximation. The calculation is repeated until the difference is within the precison required. The

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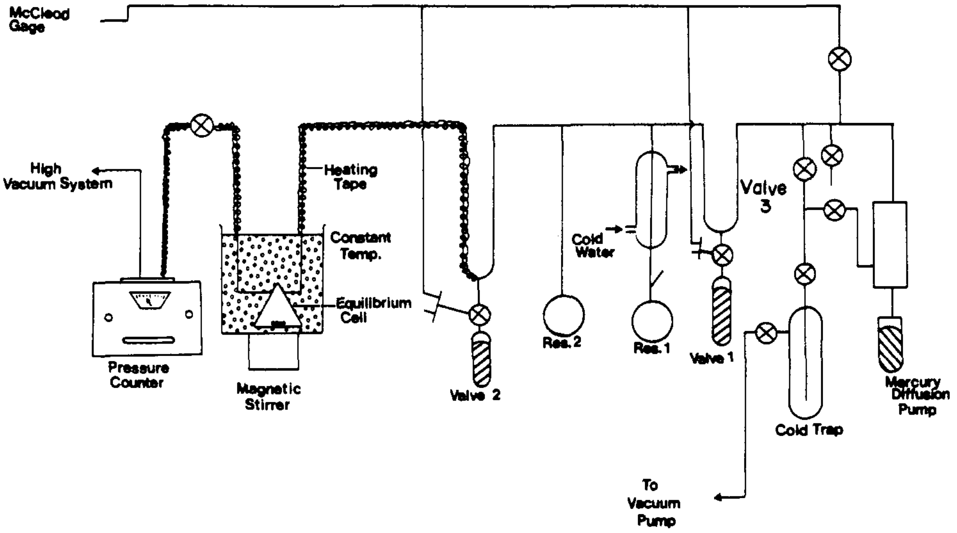

Figure 1. Schematic diagram of apparatus

Table I. Physical Properties of Materials Used at 25°C

Material	Exptl	Literature
	Refractive Index	
n-Hexane	1.37230	1.37226 (*15*)
Cyclohexane	1.42351	1.42354 (*15*)
Benzene	1.49787	1.49790 (*15*)
	Density	
n-Hexane	0.65490	0.65480 (*15*)
Cyclohexane	0.77383	0.77389 (*15*)
Benzene	0.87384	0.87368 (*15*)

Table II. Total Vapor Pressure–Liquid Composition Data for Cyclohexane–Benzene System

$x_1 = 0$		$x_1 = 0.102$		$x_1 = 0.174$		$x_1 = 0.418$	
t, °C	*P* obsd, mm Hg	*t*, °C	*P* obsd, mm Hg	*t*, °C	*P* obsd, mm Hg	*t*, °C	*P* obsd, mm Hg
6.68	38.16	0.50	29.83	0.45	31.40	0.53	32.92
7.02	38.94	2.51	33.36	3.24	36.45	6.13	44.13
9.88	45.30	6.30	40.63	5.77	41.66	10.23	54.36
10.07	45.70	10.18	49.81	9.35	50.06	14.19	66.20
11.43	49.18	13.59	59.09	12.58	58.89	17.74	78.51
12.80	52.71	16.91	69.57	17.04	73.16	21.68	94.37
13.47	54.49	20.87	83.99	21.08	88.66	25.06	109.93
15.29	59.60	25.51	104.07	24.94	105.61		
16.63	63.89						
17.97	68.13						
20.00	75.31						
20.07	75.54						
22.34	84.13						
25.05	95.59						
25.32	96.66						

$x_1 = 0.735$		$x_1 = 0.838$		$x_1 = 0.923$		$x_1 = 1.000$	
t, °C	*P* obsd, mm Hg	*t*, °C	*P* obsd, mm Hg	*t*, °C	*P* obsd, mm Hg	*t*, °C	*P* obsd, mm Hg
0.63	32.98	0.62	31.91	0.42	30.13	6.08	38.73
4.41	40.34	3.69	37.60	3.18	34.96	10.70	49.32
8.28	49.37	7.14	44.81	5.56	39.74	12.53	54.21
11.97	59.28	9.66	50.97	6.10	40.88	15.03	61.20
16.52	73.97	12.80	59.58	10.33	50.67	17.23	68.21
20.48	89.11	16.00	69.63	13.99	60.84	20.74	80.39
22.37	97.23	18.87	79.71	17.86	73.30	23.13	89.90
24.92	109.00	21.66	90.59	21.82	88.13	25.14	98.41
		25.00	105.03	25.05	102.11		

P_{calc}, y, ln γ, and G^E values are then calculated. The excess Gibbs free energies are obtained from Equation 5.

$$G^E = RT\,(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \tag{5}$$

The error introduced in the calculation by assuming $\delta_{12} = 0$ was negligible.

Direct method. This method follows the procedure described by Chang and Lu (*4*). At moderately low pressures and assuming that the vapor phase is an ideal solution, direct evaluation of equilibrium vapor compositions for binary systems at constant temperature is given by:

$$\frac{dy_1}{dx_1} = \frac{\psi y_1(1 - y_1)dP}{(y_1 - x_1)\,dx_1} \tag{6}$$

Table III. Total Vapor Pressure–Liquid Composition Data for *n*-Hexane–Cyclohexane System

$x_1 = 0.064$		$x_1 = 0.321$		$x_1 = 0.349$	
t, °C	*P* obsd, mm Hg	*t*, °C	*P* obsd, mm Hg	*t*, °C	*P* obsd, mm Hg
0.60	31.06	0.61	37.27	0.52	37.14
3.74	36.74	3.49	43.24	5.21	47.33
8.49	46.95	4.92	46.52	10.43	61.51
12.19	56.66	6.24	49.76	14.98	76.61
16.23	68.81	10.30	60.93	17.27	85.31
20.83	85.47	13.31	70.45	20.43	98.56
25.42	105.10	14.90	75.79	24.99	120.86
		17.98	87.46		
		21.41	101.98		

$x_1 = 0.504$		$x_1 = 0.736$		$x_1 = 0.850$		$x_1 = 1.000$	
t, °C	*P* obsd, mm Hg	*t*, °C	*P* obsd, mm Hg	*t*, °C	*P* obsd, mm Hg	*t*, °C	*P* obsd, mm Hg
0.48	40.46	0.37	42.80	0.57	44.81	0.43	46.41
4.35	49.51	3.41	50.15	4.18	54.04	1.64	49.48
8.26	60.31	8.32	64.24	7.93	65.39	3.53	54.68
12.43	73.98	12.53	79.04	13.06	84.25	5.65	60.77
15.77	86.60	16.53	95.63	16.13	97.13	8.05	68.79
19.46	102.69	20.67	115.52	20.51	118.82	9.93	75.43
25.02	131.63	24.93	139.52			12.56	85.77
						14.93	96.00
						17.53	108.44
						19.96	121.18
						22.33	134.56
						25.17	152.53

Table IV. Total Vapor Pressure–Liquid Composition Data for *n*-Hexane–Benzene System

$x_1 = 0.048$		$x_1 = 0.118$		$x_1 = 0.269$	
t, °C	*P* obsd, mm Hg	*t*, °C	*P* obsd, mm Hg	*t*, °C	*P* obsd, mm Hg
5.28	40.07	0.47	34.80	0.53	39.98
10.42	52.43	3.74	41.29	3.95	47.91
14.98	65.66	6.61	47.94	7.34	57.02
17.98	75.91	10.74	59.13	10.77	67.21
21.07	87.97	16.22	77.12	16.57	89.12
24.98	105.13	21.14	96.96	20.25	105.54
		24.36	112.09	24.10	125.27

$x_1 = 0.366$		$x_1 = 0.501$		$x_1 = 0.735$		$x_1 = 0.910$	
t, °C	*P* obsd, mm Hg	*t*, °C	*P* obsd, mm Hg	*t*, °C	*P* obsd, mm Hg	*t*, °C	*P* obsd, mm Hg
0.70	42.61	1.17	45.88	0.84	47.39	0.38	46.99
4.15	50.93	5.11	56.22	5.33	59.74	4.77	58.99
7.63	61.08	9.29	69.43	10.48	77.23	8.69	71.84
12.83	78.66	13.56	85.44	13.91	90.96	13.85	92.14
16.55	93.64	17.24	101.27	17.68	108.52	17.95	111.47
20.15	110.59	20.81	119.18	21.15	126.83	20.71	126.30
25.06	137.38	24.91	142.98	25.30	152.25	25.16	153.65

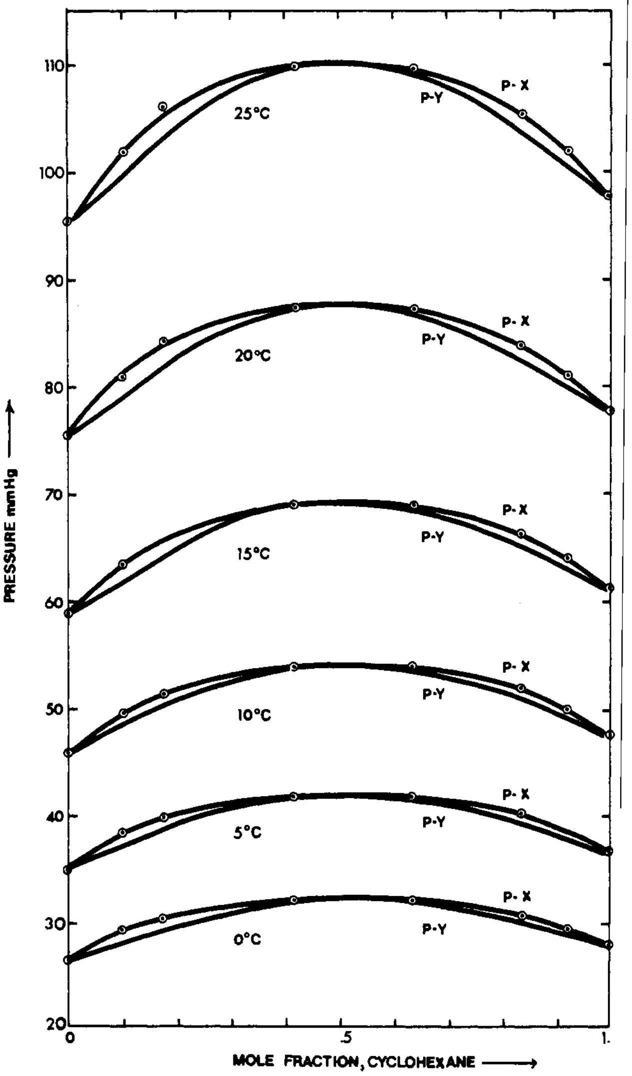

Figure 2. Total vapor pressure–composition diagram for cyclohexane–benzene system

Table VI. Redlich-Kister Constants for Correlating Liquid Activity Coefficients Obtained from Indirect Method and Deviations Obtained from Correlation

t, °C	*B*	*C*	*D*	SD,[a] mm Hg	Abs av dev, %
		Cyclohexane–benzene			
0	0.68153	−0.06759	0.13848	0.18	0.41
5	0.63873	−0.05811	0.12093	0.21	0.33
10	0.60295	−0.05241	0.10381	0.25	0.29
15	0.57340	−0.05074	0.08817	0.30	0.27
20	0.54945	−0.05269	0.07408	0.35	0.24
25	0.53045	−0.05819	0.06222	0.39	0.19
		n-Hexane–Cyclohexane			
0	0.24752	−0.10364	0.01142	0.16	0.27
5	0.22211	−0.09483	0.01935	0.18	0.21
10	0.19985	−0.08396	0.02179	0.20	0.19
15	0.17993	−0.07093	0.02123	0.22	0.18
20	0.16256	−0.05683	0.01900	0.23	0.15
25	0.14729	−0.04020	0.01352	0.30	0.16
		n-Hexane–benzene			
0	0.76000	−0.10004	0.08646	0.10	0.14
5	0.72859	−0.10314	0.06985	0.12	0.14
10	0.69871	−0.10339	0.06011	0.15	0.15
15	0.67082	−0.10235	0.05265	0.19	0.14
20	0.64442	−0.09992	0.04786	0.23	0.14
25	0.61947	−0.09652	0.04754	0.27	0.14

[a] Standard deviation = $\sqrt{\dfrac{\Sigma(\Delta P^2)}{(n-3)}}$.

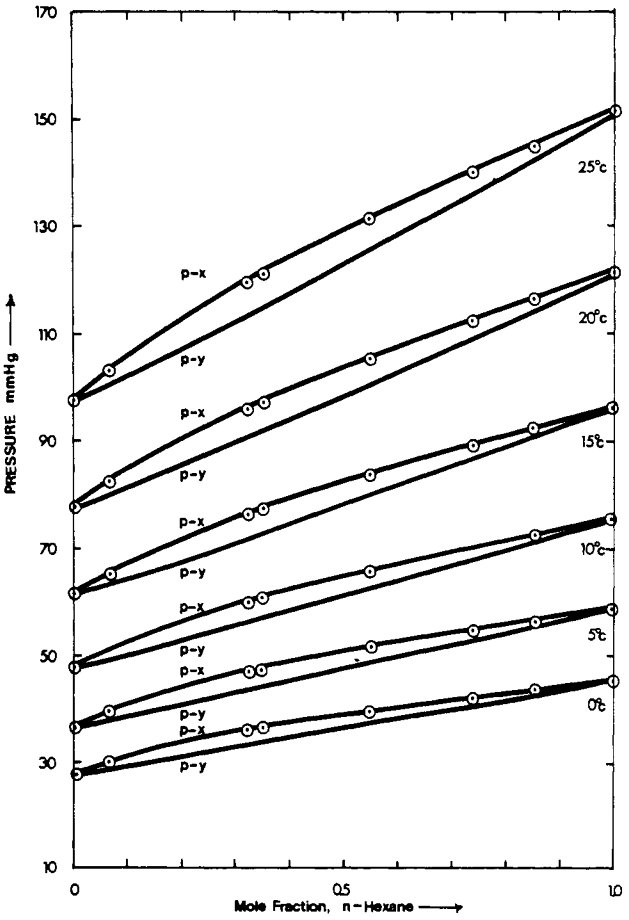

Figure 3. Total vapor pressure–composition diagram for *n*-hexane–cyclohexane system

in which

$$\psi = \frac{x_1\beta_{11} + x_2\beta_{22} - V}{RT} + \frac{1}{P} \quad (7)$$

Numerical integration of Equation 6 may proceed either from $x_1 = 0$ to $x_1 = 1$ or from $x_1 = 1$ to $x_1 = 0$.

An approximation has been used for the initial step of the integration—

$$dy_1/dx_1 = \Delta y_1/\Delta x_1 \quad (8)$$

If the integration starts at $x_1 = 0$, then

$$\Delta y_1 = (y_1)_{x_1=h} - (y_1)_{x_1=0} = (y_1)_{x_1=h} \quad (9)$$

where h is the size of the integration step. With this approximation, the y_1 value at the end of the initial step can be solved algebraically.

$$(y_1)_{x_1=h} = \left[\frac{x_1(1 + (dP/dx_1)\psi)}{1 + x_1(dP/dx_1)\psi}\right]_{x_1=h} \quad (10)$$

Similar expression can be derived for first approximation in the case that the integration proceeds from $x_1 = 1$. The subsequent points can be integrated by using the Runge-Kutta method.

The total vapor pressure-liquid composition values are correlated by the following equation:

$$P = p_1x_1 + p_2x_2 + x_1x_2\,[C_1 + C_2(x_1 - x_2) + C_3(x_1 - x_2)^2] \quad (11)$$

The quantity (dP/dx) in Equations 6 and 10 are calculated by differentiation of Equation 11. The constants C_1, C_2, and C_3 obtained for the three binary systems over the temperature range from 0° to 25°C are listed in Table 7. Results of P_{calc}, y, ln γ, and G^E values calculated by the indirect method as well as P_{calc} and y values obtained by the direct method are listed in Tables 8–10. The graphical presentation of the P-x-y values for the systems investigated are shown in Figures 2–4.

Since freezing points of mixtures are lower than those of the pure components, we were able to investigate the cyclohexane-benzene system at 0°C. The total vapor pressures of this system at 10°C were compared with the results from Boublik (*2*) (Figure 5). The agreement obtained is extremely well. As observed from Tables 8–10, the values of y and P_{calc}, calculated by both the indirect and direct methods, are in close agreement with standard deviations less than 0.006 mole fraction and 0.4 mm Hg, respectively.

In combining with some of the literature data, a new set of Antoine constants at an extended temperature range from 0° to 80°C were calculated and are given in Table 11. From these constants, the total vapor pressures at isothermal conditions and the bubble-point temperatures at isobaric conditions were calculated and compared with the literature data (*3*, *8*, *9*, *12*, *14–16*, *18*). They all agree well except the vapor pressure of pure *n*-hexane of Susarev and Chen (*18*), which is slightly higher than that of this work and that reported by Scatchard (*16*) and Dreisbach (*6*).

Azeotropes were present in the two systems containing benzene. The numerical values of the azeotropic concentration and total vapor pressure calculated by differentiation of Equation 11 and from the correlated constants are

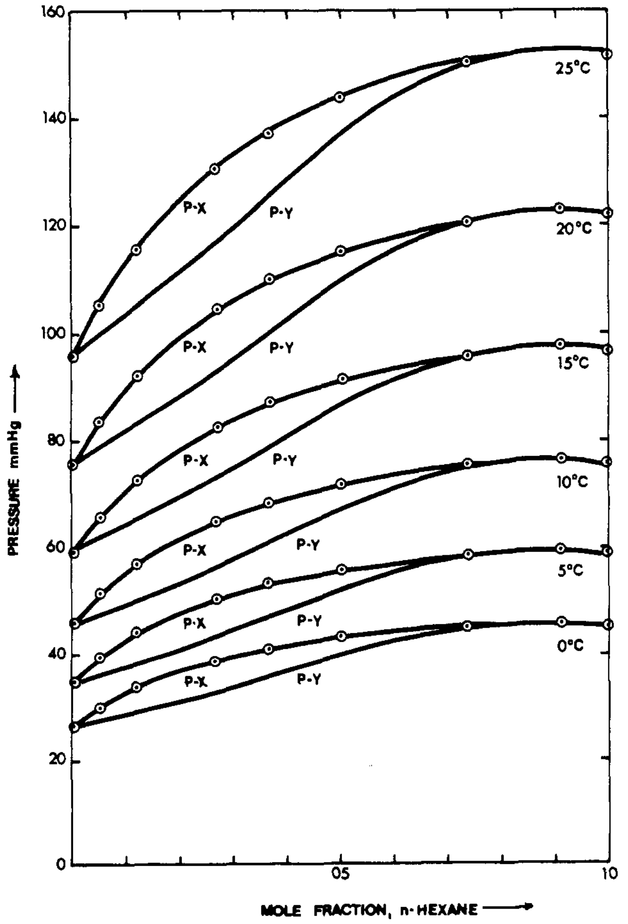

Figure 4. Total vapor pressure–composition diagram for *n*-hexane–benzene system

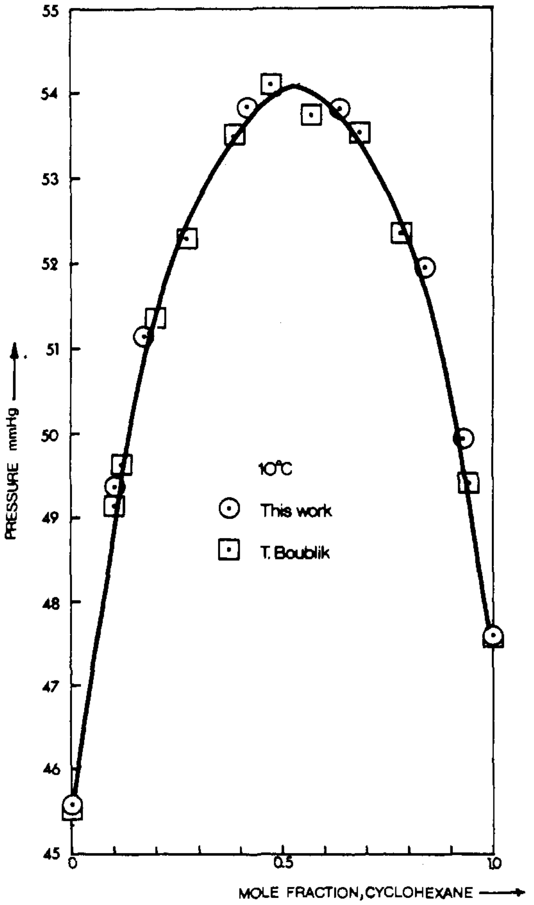

Figure 5. Comparison of total vapor-pressure values with literature data for cyclohexane–benzene system at 10°C

tabulated in Table 12. As seen from this table, the comparison of the azeotropic composition and azeotropic total vapor pressure between this work and the calculated literature values agrees well with the difference less than 0.02 mole fraction and 1.5 mm Hg, respectively.

Nomenclature

a, b, c = Antoine constants
C_1, C_2, C_3, C_4 = constants
B, C, D = Redlich-Kister parameters
G^E = Molal excess Gibbs free energy
P = total vapor pressure
p = vapor pressure of pure component
R = gas constant
T = temperature, K
t = temperature, °C
V = liquid molal volume of pure component
x = mole fraction in liquid phase
y = mole fraction in vapor phase
$\beta_{11}\beta_{22}$ = second virial coefficient of pure components 1 and 2, respectively
β_{12} = cross second virial coefficient
γ = activity coefficient
δ = defined by Equation 3

Subscripts

$1, 2, i, j$ = components
calc = calculated value

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Densities and Partial Molal Volumes of Water-Ethylene Glycol Mixtures

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Densities and partial molal volumes of water-ethylene glycol mixtures were determined at 25° and 38.5°C. The densities can be expressed in terms of fourth-degree polynomials with respect to the mole fraction of ethylene glycol. The partial molal volume of ethylene glycol had a minimum at both temperatures, occurring at the respective mole fractions 0.063 and 0.053. In the mole fraction range 0.64-0.74 ethylene glycol, the partial molal volumes were nearly constant. This might be due to the presence of hydrogen-bonded aggregates in the mixture.

In connection with a study of micelle formation in water-ethylene glycol mixtures (*7*), we determined the densities and partial molal volumes of the two-component solvent mixtures at two temperatures. These data were of interest in comparisons of the behavior of ethylene glycol and of monohydric alcohols in aqueous mixtures (*8*). Deviations from ideality in ethanol-water mixtures were related to alcohol-water interactions and to changes in liquid structure (*1*). Densities and partial molal volumes of water-ethylene glycol mixtures were determined at 25°C by Timasheff and Inoue (*9*) and at 20°C by Nakanishi (*4*), but few data points were taken at high glycol concentrations ($x_2 > 0.9$). No comparative measurements at higher temperatures are available.

Experimental

Fisher "certified" ethylene glycol was dried overnight with anhydrous Na_2SO_4, distilled in vacuum (5-mm Hg pressure, 60-65°C), and stored under dry nitrogen.

Measurements were made with a 10-ml Sprengel-type pycnometer, calibrated with distilled water at the temperatures of the measurements. Prior to weighings, it was thermostated by immersion in the main bath of a Haake model "NBe" constant-temperature circulator, regulated to within ±0.05°C. The weighings were corrected for air buoyancy.

Results

The density can be expressed as a polynomial in x_2, the mole fraction of ethylene glycol. With a least-squares fitting technique, fourth-degree polynomials gave best

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