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Vapor−Liquid Equilibria for Ethanol + Hept-1-yne and Butyric Acid + Butyric Anhydride

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Experimental (*x*, *y*, *P*) measurements of ethanol + hept-1-yne at 55 °C and 75 °C and butyric acid + butyric anhydride at 120 °C and 155 °C were obtained in an isothermal circulating glass still. The vapor pressure of hept-1-yne was measured from 43 °C to 100 °C. Ethanol + hept-1-yne exhibits moderate positive deviations from ideal behavior and a minimum-boiling homogeneous azeotrope at both temperatures. Butyric acid + butyric anhydride exhibits weak positive deviations, and no azeotrope was observed.

Introduction

Binary mixtures of alcohols and alkynes, and those of organic acids and anhydrides, have not been studied extensively. Measurements of the phase behavior of mixtures of such compounds are required for the interaction parameters between the various functional groups. Such parameters can be used in simulation packages used for the design of separation/mixing processes.

Ethanol + hept-1-yne and butyric acid + butyric anhydride were studied as part of an ongoing investigation of phase equilibrium for systems of industrial interest sponsored by Project 805/90A of the Design Institute for Physical Property Data (DIPPR) of the American Institute of Chemical Engineers, aimed at enhancing the understanding of interactions of functional groups. Results from these studies have been used for filling gaps in the group-interaction matrices of generalized correlations such as ASOG and UNIFAC. The data are also useful in supporting specific design applications.

Experimental Section

USP grade ethanol, dehydrated to 200 proof, was purchased from Pharmaco. Hept-1-yne, 99+% purity, was purchased from Aldrich. Analysis by gas liquid chromatography (GLC) indicated that the purity was 99.45%. Butyric acid and butyric anhydride with 99% purity were purchased from Aldrich and were used without further purification. All reagents were stored in desiccators after opening. The properties of the pure components are given in Table 1.

Table 1. Properties of Pure Components

compd	ethanol	hept-1-yne	butyric acid	butyric anhydride
fw	46.07	96.17	88.11	158.20
melting temp, t_m/K	−114	−81	−5.3	−73.4
boiling temp, t_B/°C	78.25	99.75	163.2 163.27[a]	197.7 197.78[a]
ρ(20°C)/(g·cm^{-3})	0.790	0.7332	0.956	0.967

[a] This work. All other values from DIPPR Project 801.

The isothermal, circulating glass cell, shown in Figure 1, has been previously used for measurements at Columbia University and in other laboratories (Zudkevitch et al., 1989, 1990; Zudkevitch, 1992). This miniature equilibrium cell was specifically designed for obtaining thermodynamically consistent vapor−liquid equilibrium (VLE) results at pressures below 100 kPa using only small quantities of relatively hard-to-obtain samples at, as close as possible, isothermal conditions. The liquid is stirred magnetically, and the vapor dome is heated by an external coating of conducting film (Instatherm). With three separate automatically controlled heating circuits, practically uniform temperature was maintained inside the entire cell. This feature differentiates this cell's operation from those of most condensate-circulating cells in which the temperature of the vapor, which is usually colder than the liquid, is reported (Othmer et al., 1960).

The cell has two additional heating circuits which are used for heating the condensate's return tube and the liquid sampling septum, as well as the drain's tube and stopcock. These heaters, as well as circulation of warm water in the condenser, were not used in this study but had been used in other studies to prevent precipitation of relatively high melting compounds, such as phenol, in any part of the system.

During an experiment, the three-way stopcock of the condensate is turned open so that the liquid flows continuously back into the still. After equilibration is reached and the sample is to be taken, the three-way stopcock is turned to allow a small quantity of the condensate (about 0.1 cm^3 or less) to accumulate above the stopcock. The main (liquid) heater is turned off. The vacuum pump is turned off to stop further vaporization, and the vent and the condensate septum are opened to break the vacuum. Then a sample is drawn with a syringe whose long needle (75 mm) is inserted through the septum's stopcock's capillary to reach the condensate accumulated above the three-way stopcock. Following sampling, the septum's stopcock is turned shut and the three-way condensate stopcock is returned for resuming total circulation.

This procedure minimizes the condensate holdup and, hence, depletion of the volatile compound from the liquid. In a similar manner, liquid samples are taken with a syringe whose long needle is inserted through the capillary of the liquid-sampling septum's stopcock. An additional advantage of this apparatus is that, due to its size, it allows

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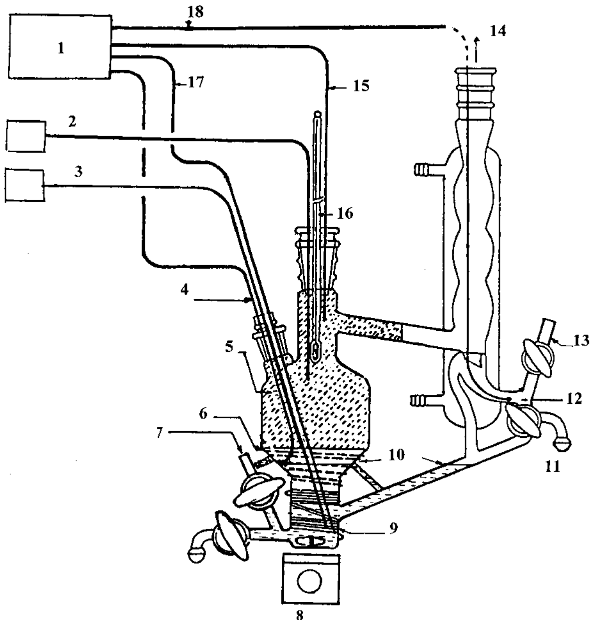

Figure 1. Schematic diagram of vapor−liquid equilibrium apparatus: (1) digital temperature indicator; (2) controller for heater H_3; (3) controller for heater H_1; (4) glass temperature at interface; (5) H_3, instatherm heating coating for vapor space; (6) H_2, heater for interface; (7) liquid sampling; (8) magnetic stirrer/heater; (9) H_1, liquid heater/boiler; (10) liquid level; (11) three-way stopcock; (12) vapor condensate; (13) vapor sampling septum; (14) to second condenser, traps and pressure control and measurement; (15) vapor temperature indicator; (16) precision thermometer; (17) liquid temperature indicator; (18) condensate temperature indicator.

the fluid inside to respond quickly to the temperature and pressure controls.

The cell is charged with about 40 cm^3 of a liquid mixture. In operation, the pressure is set at the estimated level for the solution's composition at the experiment's lower temperature, e.g. 55 °C for the ethanol + hept-1-yne system. Then the controllers are set and the heaters turned on. The controllers are set so that the vapor is kept at a temperature which is either the same or slightly higher (about 0.5 K) than that of the liquid. Fine-tuning (and gross control) of the liquid temperature is achieved by manually controlling the system's pressure. The heat input (controlled by the powerstats) is set to maintain a vaporization/condensation rate of 5−10 drops/min. Equilibrium was usually reached in about 20 min after the temperature and pressure had stabilized.

When equilibrium was reached, all conditions, pressure (two manometers and a McLeod gauge), temperature (read from the five thermocouples), and settings, were recorded. As described above, the three-way condensate stopcock was turned to allow a little condensate to accumulate and samples were taken with syringes for injection into the GLC for analysis. At least two samples of each phase of a nominal liquid composition were analyzed to ensure reproducibility. On several occasions, the system was restarted and another set of samples were taken when equilibrium was reached. Following that, the temperature and pressure settings were changed to those of the higher experimental temperature, 75 °C for the first binary and 155 °C for the second, and the entire procedure was repeated. When it was deemed necessary, predetermined amounts of liquid were withdrawn from the cell to be replaced by predetermined pure liquids to make the next desired composition.

Analyses were carried out with a thermal conductivity detector in a Hewlett-Packard TC 5830 GLC, using a 1 m × $^1/_4$ in. o.d. stainless steel column filled with Porapack-SP adsorbant, and 0.5 cm^3 samples of the liquid were injected. The analytical operation was temperature programmed, and the chromatography data, in area percent, were converted to concentrations in mole percent. Standard samples of known compositions were prepared and a calibration curve was plotted to establish a correlation for the plot of area percent values from the GLC as a function of compositions in mass percent.

Analysis

Redlich and Kister (1948) proposed a thermodynamic consistency test which compares the negative and positive parts of the integral of $\log(\gamma_1/\gamma_2)$ as a function of x_1, the mole fraction of component 1. The Redlich−Kister equal area test for a set of binary data is based on the integral form of the Gibbs−Duhem equation. At a constant temperature this integral is

$$\int_0^1 \log\,(\gamma_1/\gamma_2)\,\partial x_1 + \int_0^1 (V^E/RT)\,(\partial P/\partial x_1)_T\,\partial x_1 \qquad (1)$$

where γ_1 and γ_2 are the activity coefficients of components 1 and 2, respectively, at x_1, the mole fraction of component 1 and V^E is the excess volume. The effect of V^E is normally neglected. Gilmont et al. (1950) proposed a correlation which is essentially equivalent to the Redlich−Kister equation; a second-order truncated form of the equation was later used by Gilmont et al. (1961).

$$\log(\gamma_1/\gamma_2) = g'X + g''[X^2 - {}^1/_{12}] \qquad (2)$$

where $X = (x_2 - x_1)/2$. Equation 2 has been found adequate for describing complex mixtures. The correlation parameters, g' and g'' were established by the method of weighted least squares. Values of $\log(\gamma_1/\gamma_2)$ were also plotted in order to determine if additional measurements were required.

The coefficients A_{12}, B_{12}, A_{21}, and B_{21} of the three suffix Margules equation,

$$\log \gamma_1 = A_{12}{x_2}^2 + B_{12}{x_2}^3 \qquad (3)$$

$$\log \gamma_2 = A_{21}{x_1}^2 + B_{21}{x_1}^3 \qquad (4)$$

are related to the coefficients g' and g'' by

$$A_{12} = 0.5(g' - g'') \qquad (5)$$

$$B_{12} = 2(g'')/3 \qquad (6)$$

$$A_{21} = 0.5(g' + g'') \qquad (7)$$

$$B_{21} = -2g''/3 \qquad (8)$$

The calculated vapor pressure P(calc) and vapor mole fraction y_1(calc) values in Table 4 were calculated from the vapor pressure data and activity coefficients derived for the Margules equation and the coefficients of eqs 3 and 4.

Evaluation of Data for Mixtures with Associating Compounds. Mixtures containing water, alcohols, carboxylic acids, and phenols exhibit association in the fluid phases which influences the equilibrium calculations. The large deviations of compounds with hydrogen bonding from ideal behavior has been attributed to the formation of dimers and higher polymers, especially in the vapor phase. For acids it has been suggested that the only important multimer is the ring dimer:

Table 2. Vapor Pressures of Pure Components

	$P°$/kPa			
t/°C	ethanol	hept-1-yne	butyric acid	butyric anhydride
55.0	37.40[a]	20.14[a]		
	37.48[b]	21.52[c]		
75.0	88.77[a]	43.93[a]		
	88.82[b]	45.35[b]		
120			22.18[a]	7.39[a]
			22.08[b]	8.37[b]
155.0			78.29[d]	
			78.58[a]	28.86[a]
			77.4[b]	29.46[b]
163.2			101.74	

[a] This study. [b] DIPPR 801 equation. [c] TRC, 1998.

Marek and Standart (1954) proposed the following expressions for association.

$$Py_2Z_2 = P_2°x_2y_2\Gamma_2 \tag{9}$$

where $P_2°$ is the vapor pressure of component 2 and Z_2 and Γ_2 are the correction factors for association in the vapor and liquid, respectively, and are given by

$$Z_2 = \{1 + (1 + 4K_0P_2°)^{0.5}\}/[1 + \{4KPy_2(2 - y_2)\}^{0.5}] \tag{10}$$

where K_0 is the association constant at the vapor pressure $P_2°$, K is the association constant at the mixture pressure P, and

$$\Gamma_2 = \{1 + (1 + 4K)^{0.5}\}/[1 + \{1 + 4Kx(2 - x)\}^{0.5}] \tag{11}$$

Jenkins and Gibson-Robinson (1977) and Nagata and Tamura (1991) have suggested that eqs 9−11 cannot be neglected in the vapor phase and that dimerization effects are also significant for the liquid phase. In those studies, results for mixtures of carboxylic acids with nonpolar, nonsolvating compounds were fitted with the NRTL equation of Renon and Prausnitz, (1968) with additional terms for the interactions of monomers, dimers, and miltimers. The tabulated and plotted results suggest that, unless dimerization in the liquid phase is expressed as a function of composition, systematic deviations from consistency should be expected.

Tsonopoulos and Prausnitz (1970), using data of Lundin et al. (1952), proposed the following equations for the dimerization and trimerization of butyric acid in the vapor phase:

$$\log K(\text{dim.}) = 10.1{-}3040(T/\text{K}) \tag{12}$$

$$\log K(\text{tri}) = 18.45{-}5020(T/\text{K}) \tag{13}$$

The above approach requires additional information about the equilibria in the mixture which is not available. Consequently, the effect of association on the mixture behavior was not considered in this study, and only the activity coefficients derived from raw (P, x, y) data are presented.

Results, Analysis, and Correlation of Data

The melting point, boiling point, and density of the pure components are given in Table 1, and the vapor pressures are given in Table 2. New data on the vapor pressure of hept-1-yne were measured as part of this study. They are presented in Table 3.

Ethanol (1) + Hept-1-yne (2). The measured vapor pressures of hept-1-yne from 43 °C to 100 °C are given in Table 3, where they are compared with evaluated data from the Thermodynamics Research Center (TRC, 1998). The evaluated values are based primarily on the low-temperature results of Letcher and Baxter (1987) and the higher temperature results of Eisen and Orav (1970). The differences are significant in the range 50 °C to 90 °C but are in good agreement in the vicinity of the boiling point.

Table 3. Vapor Pressure of Hept-1-yne (This Work)

t/°C	P/kPa	P(lit.)[a]/kPa	t/°C	P/kPa	P(lit.)[a]/kPa
43.4	13.07	13.23	84.6	61.14	62.83
47.5	14.54	15.79	90.0	73.32	74.71
55.0	20.13	21.52	92.6	79.89	81.03
62.7	27.84	29.07	99.9	100.71	101.06
69.0	35.36	36.73	100.2	101.52	101.96
75.0	43.93	45.46			

[a] TRC, 1998.

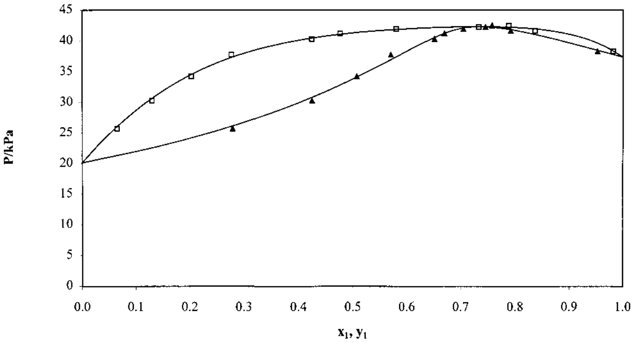

Figure 2. Experimental P, x, y results for ethanol + hept-1-yne at 55 °C: ○, liquid; ●, vapor. Full line calculated from eqs 3 and 4.

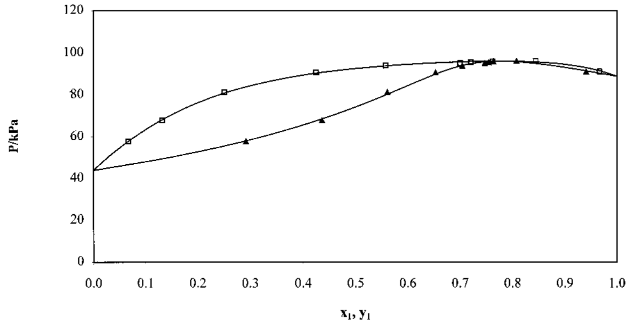

Figure 3. Experimental P, x, y results for ethanol + hept-1-yne at 75 °C: ○, liquid; ●, vapor. Full line calculated from eqs 3 and 4.

At both temperatures, this system exhibits strong positive deviations from ideal behavior, and azeotropes were observed. Ratios of activity coefficients were curve-fitted with eq 2, and the data were considered consistent. The ratios were also plotted and extrapolated to infinite dilution. The infinite dilution activity coefficients were compared with the values obtained from the regression.

The calculated pressure and vapor composition are given in Table 4 and shown graphically in Figures 2 and 3. In making the comparisons, attention was drawn to the small variations in the temperatures of the individual experiments.

Butyric Acid (1) + Butyric Anhydride (2). The vapor pressures of the pure components were measured at the nominal temperatures of the isothermal VLE studies. The values for butyric acid and butyric anhydride are given in Table 2, which also includes a summary of relevant physical properties.

(P, x, y) values obtained at 120 °C and 155 °C are given in Table 5 and are shown in Figures 4 and 5. In analyzing

Table 4. Experimental Vapor−Liquid Equilibrium Data for Ethanol + Hept-1-yne and Butyric Acid + Butyric Anhydride[a]

t/°C		P/kPa	P(calc)/kPa	x_1	y_1	y_1 (calc)	γ_1 (expt)	γ_2 (expt)
liquid	vapor							
Ethanol (1) + Hept-1-yne (2)								
55	55.2	25.73	25.51	0.0653	0.2792	0.2594	2.9414	0.9857
55	55.0	30.33	31.05	0.1299	0.4249	0.4269	2.6529	0.9958
55	55.0	34.29	35.00	0.2028	0.5073	0.5225	2.2937	1.0527
55	55.1	37.78	37.81	0.2767	0.5703	0.5828	2.0824	1.1150
55	55.2	40.34	40.94	0.4248	0.6514	0.6512	1.6542	1.2145
55	55.1	41.25	41.53	0.4768	0.6698	0.6666	1.5495	1.2932
55	55.2	41.96	42.26	0.5803	0.705	0.6916	1.3630	1.4649
55	55.0	42.26	42.67	0.7334	0.7455	0.7314	1.1488	2.0041
55	55.1	42.53	42.57	0.7876	0.7575	0.7524	1.0938	2.4120
55	55.3	41.66	42.27	0.8370	0.7916	0.7789	1.0537	2.6460
55	55.0	38.32	38.50	0.9814	0.9526	0.9541	0.9946	4.8405
estd azeotrope								
55.0			42.58		0.7619	0.7619		
75	75.2	57.78	58.11	0.0670	0.2915	0.2917	2.8342	1.0004
75	75.2	67.83	68.50	0.1319	0.4357	0.4336	2.5270	1.0053
75	75.0	81.26	81.16	0.2506	0.5603	0.5668	2.0492	1.0870
75	75.1	90.69	90.53	0.4248	0.6527	0.6576	1.5716	1.2483
75	75.0	93.92	93.90	0.5576	0.7038	0.6996	1.3372	1.4337
75	75.1	95.06	95.76	0.6998	0.7469	0.7437	1.1443	1.8273
75	75.2	95.46	95.91	0.7201	0.7542	0.7512	1.1250	1.9252
75	75.2	95.94	96.07	0.7617	0.7631	0.7684	1.0840	2.1747
75	75.1	96.14	95.68	0.8439	0.8069	0.8139	1.0368	2.7113
75	75.0	91.07	91.45	0.9658	0.9398	0.9393	0.9996	3.6505
estd azeotrope								
75.0			96.26		0.7830	0.7830		
Butyric Acid (1) + Butryic Anhydride (2)								
120.0	120.0	9.35	9.23	0.0673	0.2620	0.2507	1.6400	1.0012
120.0	120.2	9.69	9.87	0.0946	0.3126	0.3177	1.4436	0.9963
120.0	120.2	11.69	11.76	0.1891	0.5032	0.4775	1.4025	0.9698
120.0	120.1	13.67	13.80	0.3190	0.6003	0.6112	1.1592	1.0859
120.0	120.2	14.26	14.72	0.3872	0.6826	0.6638	1.1336	1.0004
120.1	120.0	16.28	16.65	0.5416	0.7707	0.7632	1.0441	1.1025
120.0	120.0	18.14	18.17	0.6687	0.8352	0.8349	1.0216	1.2219
120.0	120.3	18.90	18.70	0.7137	0.8624	0.8591	1.0297	1.2302
120.0	120.0	19.01	19.29	0.7630	0.8877	0.8850	0.9970	1.2197
120.0	120.2	19.68	20.11	0.8306	0.9226	0.9195	0.9853	1.2173
120.1	120.2	21.17	21.26	0.9253	0.9667	0.9657	0.9970	1.2778
120.0	120.1	21.20	21.47	0.9421	0.9726	0.9736	0.9864	1.3594
120.0	120.2	21.48	21.55	0.9485	0.9788	0.9766	0.9991	1.1975
120.0	120.0	21.74	21.62	0.9543	0.9766	0.9793	1.0030	1.5104
155.0	155.1	32.93	33.69	0.0594	0.2086	0.1927	1.4544	0.9612
155.0	155.2	34.06	34.42	0.0692	0.2236	0.2176	1.3843	0.9857
155.1	155.0	42.30	42.98	0.2013	0.4619	0.4529	1.2208	0.9888
155.0	155.0	48.56	49.19	0.3187	0.5893	0.5815	1.1292	1.0155
155.0	155.3	52.53	53.39	0.4075	0.6714	0.6564	1.0885	1.0107
155.0	155.1	58.99	59.32	0.5426	0.7592	0.7512	1.0381	1.0775
155.0	155.1	64.79	64.48	0.6647	0.8388	0.8258	1.0283	1.0807
155.0	155.0	70.79	71.47	0.8317	0.9215	0.9174	0.9876	1.1469
155.0	155.2	72.91	72.08	0.8462	0.9232	0.9249	1.0004	1.2632
155.0	155.0	74.54	74.98	0.9150	0.9607	0.9595	0.9843	1.1957
155.0	155.3	76.61	76.45	0.9497	0.9754	0.9764	0.9895	1.3024

[a] γ_1 and γ_2 were derived from the experimental data.

the data for thermodynamic consistency, the stoichiometric compositions were used to calculate apparent activity coefficients. The VLE data are presented together with their corresponding activity coefficients in Table 4.

The logarithms of the ratios of the activity coefficients were curve-fitted with eq 2 and were plotted for consistency testing, smoothing, and extrapolating to infinite dilution. These activity coefficients at infinite dilution were compared with the values obtained from regressions. Selected correlation parameters are given in Table 5.

At both temperatures, this mixture exhibits weak positive deviations from ideal mixing and no azeotropes were observed. For this system, the pressures and vapor compositions predicted without correcting for association are systematically different from the experimental data. This is especially so at 155 °C.

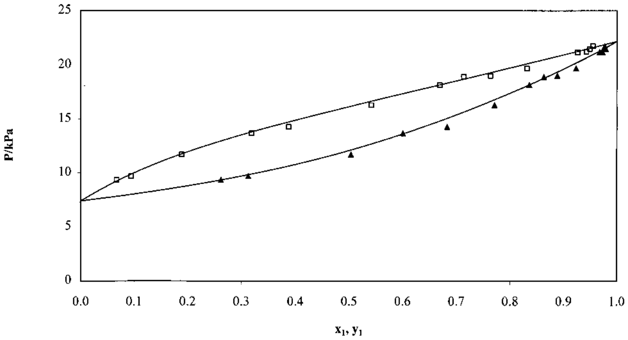

Figure 4. Experimental *P*, *x*, *y* results for butyric acid + butyric anhydride at 120 °C: ○, liquid; ●, vapor. Full line calculated from eqs 3 and 4.

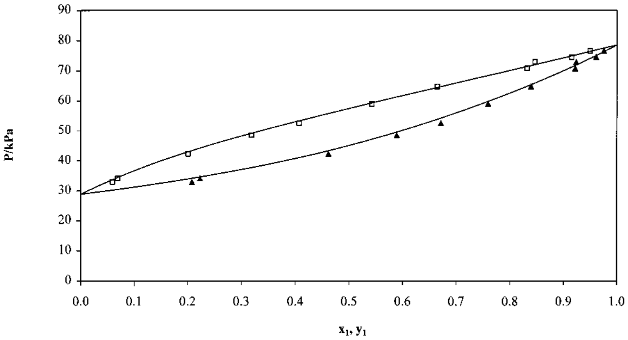

Figure 5. Experimental *P*, *x*, *y* results for butyric acid + butyric anhydride at 155 °C: ○, liquid; ●, vapor. Full line calculated from eqs 3 and 4.

Table 5. Coefficients for Correlating the Activity Coefficients for the Systems Ethanol (1) + Hept-1-yne (2) and Butyric Acid (1) + Butyric Anhydride (2) for Given Temperature (°C)

correlation coeff	ethanol (1) + hept-1-yne (2)		butyric acid (1) + butyric anhydride (2)	
	55 °C	75 °C	120 °C	155 °C
g'_{12}	1.2361	1.1236	0.3536	0.2687
g'_{12}	−0.5276	−0.3244	0.3246	0.2176
$\gamma_{12}\infty$	3.39	3.22	1.71	1.48
$\gamma_{21}\infty$	5.08	4.13	1.33	1.25
Margules				
A_{12}	0.8818	0.7230	0.0170	0.0256
B_{12}	−0.3517	−0.2149	0.2164	0.1450
A_{21}	0.3542	0.4006	0.3416	0.2431
B_{21}	0.3517	0.2149	−0.2164	−0.1450

To verify that the discrepancies are systematic, additional measurements were made. The observed systematic discrepancies, especially in predicting the total pressure, may be attributed to the failure to account for the effects of association, which can be significant.

Summary

Mixtures of ethanol and hept-1-yne exhibit smaller positive deviations from ideal behavior than those of ethanol + heptane (Van Ness et al., 1967), hex-1-ene + ethanol (Lindberg and Tassios 1971), and 1-propanol + styrene (Malyusov et al., 1957). This mixture has minimum boiling azeotropes at both temperatures.

The binary butyric acid + butyric anhydride exhibits small positive deviations from ideal behavior. These deviations are somewhat smaller than those exhibited by acetic acid + acetic anhydride (Jones, 1962). The use of stoichiometric mole fractions and apparent activity coefficients in correlating the data may be the cause for the differences between the calculated and measured total pressures.

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