and pressure. The factor $P_{\text{bubbler}}/[P_{\text{bubbler}} - \sum P_i]$ accommodates the increase in the mole flow rate due to the saturation of the He flow with the partial pressures above the compound. The mass flow rate of a single gas-phase species i is calculated by multiplying the total mole flow rate by the mole fraction and the molecular weight of component i. The total mass flow rate of the multicomponent gas mixture is then shown by

$$\text{total mass flow rate} = \frac{dm}{dt} = \frac{F_{\text{He}}}{V/n} \frac{\sum_i (P_i M_i)}{P_{\text{bubbler}} - \sum_i P_i} \qquad (3)$$

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Total Pressure Measurements for *n*-Pentane–Methanol–2-Butanol at 303.15 K

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The total pressure is reported as a function of liquid-phase composition for *n*-pentane–methanol–2-butanol and each of its constituent binary systems at 303.15 K. The data were reduced by using Baker's method. The modified Margules equation was found to fit the binary measurements adequately. The ternary measurements were modeled with an expression for the excess Gibbs free energy which includes contributions from the binary systems plus additional terms containing ternary parameters.

Introduction

Recently, renewed interest is being shown in solution models which invoke chemical equilibria to model hydrogen bonding between associating species. In these models, a component that is known to exhibit hydrogen bonding is assumed to exist as a distribution of *n*-mers in solution. If several associating species are present in a mixture, each forms *n*-mers with the other associating species in addition to itself. To test solution models which account for cross association, it is important that experimental data be available for systems which contain more than one associating component.

The present work reports total pressure measurements for *n*-pentane–methanol–2-butanol and its constituent binary at 303.15 K and is part of a larger study involving mixtures of two associating species and one nonpolar diluent. In an earlier study (*1*), total pressure data were reported for the ethanol–*n*-heptane–2-methyl-1-propanol system.

Experimental Section

***Apparatus and Procedure*.** The apparatus and procedure have been described previously (*1*). Briefly, the apparatus is of the Van Ness type (*2*), in which, for binary measurements, each pure chemical is stored in a piston injector. A portion of one of the components is metered into the equilibrium cell, and its vapor pressure is determined. Measured amounts of the second component are then added, and the total pressure is recorded after each addition. After approximately half of the composition range is covered, the equilibrium cell is emptied and charged with a measured amount of the second component, and successive amounts of the first component are added until the entire composition range is covered. The two sides of the isotherms are made to overlap at one or more compositions to check the internal consistency of the results.

For ternary measurements, one of the piston injectors is filled with pure *n*-pentane and the other is filled with a gravimetrically prepared mixture of methanol and 2-butanol. The procedure is the same as that for a binary system with the result that the overall composition in the equilibrium cell for a given run follows a straight line on a triangular diagram between the *n*-pentane (1) vertex and the composition of the methanol–2-butanol mixture. The methanol (2)–2-butanol (3) mixtures are characterized by the parameter C'

$$C' = \frac{z_2}{z_2 + z_3} \qquad (1)$$

where z_2 and z_3 are the overall mole fractions of methanol and 2-butanol in the equilibrium cell. Three different values of C' (0.2459, 0.5087, and 0.7562) were examined in this work.

The temperature of the water bath in which the equilibrium cell is suspended is controlled to within 0.02 K. Accuracy of the pressure measurements (not including the effect of variations in bath temperature) is within 0.1%. Volumes of each component displaced into the equilibrium cell were converted to moles by using saturated liquid density data at room temperature. Saturated liquid density information for *n*-pentane was taken from ref 3, while that for methanol and 2-butanol was obtained from ref 4. For the ternary system measurements, excess volumes given by Polak et al. (*5*) were used to calculate the densities of the methanol–2-butanol mixtures in the piston injector. The maximum uncertainty in the reported

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Table I. Comparison of Pure-Component Average Vapor Pressures P_i° at 303.15 K Measured in the Present Study to Literature Data

substance	P_i°/kPa present work	P_i°/kPa literature	ref
n-pentane	82.01	81.99	13
methanol	21.88	21.87	14
2-butanol	3.27	3.39	14

Table II. Saturated Liquid Volumes V_i^L and Second Molar Virial Coefficients B_{ij} Used for *n*-Pentane (1)-Methanol (2)-2-Butanol (3) at 303.15 K

	n-pentane	methanol	2-butanol
$V_i^L/(\mathrm{cm^3\ mol^{-1}})$	117.1	41.0	92.9
$B_{ii}/(\mathrm{cm^3\ mol^{-1}})$	-1172	-1840	-4381

$B_{12}/(\mathrm{cm^3\ mol^{-1}}) = -666$; $B_{13}/(\mathrm{cm^3\ mol^{-1}}) = -972$; $B_{23}/(\mathrm{cm^3\ mol^{-1}}) = -2922$

Table III. Total Pressure P as a Function of Liquid-Phase Mole Fraction x_i for the Binary Systems of *n*-Pentane (1)–Methanol (2)–2-butanol (3) at 303.15 K

n-pentane (1)–methanol (2)		*n*-pentane (1)–2-butanol (3)		methanol (2)–2-butanol (3)	
x_1	P/kPa	x_1	P/kPa	x_2	P/kPa
0.0000	21.88	0.0000	3.28	0.0000	3.27
0.0257	52.38	0.0300	12.87	0.0309	3.75
0.0565	72.89	0.0680	23.17	0.0705	4.39
0.0960	86.19	0.0966	29.76	0.1101	5.05
0.1365	92.78	0.1453	39.08	0.1496	5.71
0.1769	96.02	0.1945	46.54	0.1998	6.60
0.2273	97.93	0.2438	52.48	0.2496	7.49
0.2779	98.77	0.2955	57.40	0.2993	8.43
0.2780	98.75	0.3457	61.21	0.3495	9.39
0.3374	99.17	0.3963	64.34	0.3994	10.36
0.3977	99.35	0.3967	64.33	0.4492	11.33
0.4572	99.42	0.4465	66.90	0.4994	12.36
0.5183	99.47	0.4465	66.86	0.5495	13.35
0.5778	99.50	0.4960	68.98	0.5996	14.36
0.6388	99.53	0.4971	69.09	0.6495	15.35
0.6999	99.58	0.5456	70.83	0.6498	15.39
0.7483	99.62	0.5480	70.99	0.6996	16.33
0.8018	99.63	0.5960	72.51	0.7497	17.28
0.8487	99.59	0.5986	72.69	0.7999	18.23
0.9022	99.31	0.6461	74.01	0.8496	19.15
0.9427	98.54	0.6959	75.39	0.8988	20.05
0.9694	97.10	0.7467	76.71	0.9396	20.78
0.9865	94.01	0.7958	77.91	0.9698	21.30
1.0000	82.01	0.8469	79.03	1.0000	21.89
		0.8981	80.10		
		0.9283	80.78		
		0.9699	81.58		
		1.0000	82.03		

compositions is conservatively estimated to be 0.001 in mole fraction at the midrange of composition and 0.0005 at the extremes.

Materials. The *n*-pentane and methanol used in this study were purchased from Aldrich Chemical (HPLC grade) and have minimum purities of 99.5 and 99.97%, respectively. Anhydrous 2-butanol (99+%) was purchased from Aldrich. The specific lot used in this study was quoted by Aldrich to have a purity of 99.5%. Each pure component was degassed by the procedure discussed previously (*1*). No further attempt to purify the chemicals was made.

An indication of the purity of the substances used in this study is given by a comparison of measured vapor pressures with those in the literature, as shown in Table I. The measured values given in Table I are averaged over five measurements for *n*-pentane and two measurements for methanol and 2-butanol. The spread among measured values was 0.08 kPa for *n*-pentane and 0.01 kPa for each of the alcohols. Since the materials were degassed as needed, there may be small variations in the purity of the samples used for each run. However, the spreads in the measured values are within the uncertainties quoted earlier. Agreement with literature data is quite good.

Data Reduction

Data reduction proceeded as indicated earlier (*1*). Barker's method (*6*), in which the sum of the squares between the measured and calculated pressures is minimized, was used to obtain parameters in the assumed model for the excess molar Gibbs free energy G^E and to calculate the mole fractions of the liquid and vapor phases. With the exception of *n*-pentane–methanol, which will be discussed shortly, all regressions were unweighted. The two-term virial expansion in pressure was used to model vapor-phase nonidealities, and the Poynting corrections were also made. Second molar virial coefficients B_{ij} were calculated with use of the correlation of Tsonopoulos (*7*), and pure liquid molar volumes V_i^L at 303.15 K were obtained from the same sources used for the room-temperature liquid densities. This auxiliary information is presented in Table II.

The raw experimental data yield overall mole fractions z_i within the equilibrium cell. Although these are quite close to the liquid-phase mole fractions for the conditions of this experiment, the true liquid-phase mole fractions x_i are calculated simultaneously with the data regression, as described in ref 1. Briefly, for a current set of parameters in the model for G^E, all mass is assumed to be in the liquid phase. Vapor-phase mole fractions and pressure are obtained from bubble-point calculations for each liquid-phase composition, and, from a knowledge of the vapor volume in the equilibrium cell (obtained from the known total volume and the known volume of liquid in the cell), the moles of each component in the vapor phase are computed. The liquid-phase compositions are adjusted by mass balances, and bubble-point calculations are repeated until the liquid-phase mole fractions stabilize.

The modified Margules equation proposed by Abbott and Van Ness (*8*)

$$\left(\frac{G^E}{RT}\right)_{ij} = x_i x_j \left[A_{ji} x_i + A_{ij} x_j - \frac{\alpha_{ij} \alpha_{ji} x_i x_j}{\alpha_{ij} x_i + \alpha_{ji} x_j + \eta_{ij} x_i x_j} \right] \quad (2)$$

was used to model the binary systems examined in this study. For the methanol (2)–2-butanol (3) system, the parameter η_{23} was set equal to zero. The excess Gibbs free energy for the ternary system was assumed to have the form advanced by Abbott et al. (*9*)

$$G^E/RT = (G^E/RT)_{12} + (G^E/RT)_{13} + (G^E/RT)_{23} + F(x_1, x_2, x_3) \quad (3)$$

where the expressions for $(G^E/RT)_{ij}$ are given by eq 2 for each binary pair.

An adequate fit to the ternary data was obtained with a function F having the form

$$F = x_1 x_2 x_3 \left[C_0 - \sum_{i=1}^{3} \frac{x_i}{\sum_{j=1}^{3} C_{ij} x_j} \right] \quad (4)$$

Equation 4 contains 10 ternary parameters (C_0, C_{ij}) that must be obtained from ternary data. Simpler forms for the function F, such as those for case 1 and case 2 in ref 1, did not provide an adequate fit to the data.

Results

Total pressure data for the binary systems are given in Table III, and the P–x–y curves are shown in Figures 1–3. The

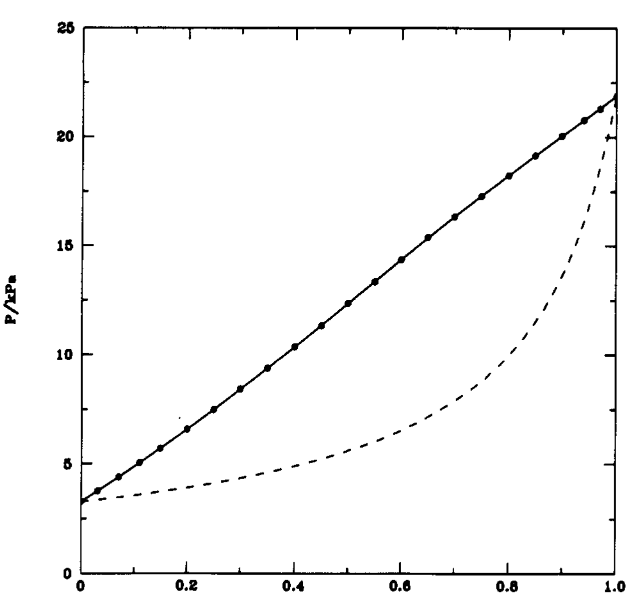

Figure 1. Pressure P vs liquid-phase mole fraction x_2, or vapor-phase mole mole fraction y_2, for methanol (2)–2-butanol (3) at 303.15 K. The points are experimental results, the solid curve is a fitted $P-x$ result, and the dashed curve is a predicted $P-y$ result.

Table IV. Coefficients A_{ij}, α_{ij}, and η_{ij} in Equation 2 for the Binary Systems of *n*-Pentane (1)–Methanol (2)–2-Butanol (3) at 303.15 K, Average Deviations ΔP_{av}, and Maximum Deviations ΔP_{max}[a]

i,j	A_{ij}	α_{ij}	η_{ij}	ΔP_{av}/kPa	ΔP_{max}/kPa
1,2	2.933 64	3.685 82	21.135 23	0.11	0.73
2,1	4.297 83	21.969 81	21.135 23		
1,3	1.484 46	1.514 40	0.815 82	0.03	0.09
3,1	3.158 34	13.509 50	0.815 82		
2,3	−0.139 97	0.183 38		0.01	0.03
3,2	0.032 83	0.269 90			

[a] $\Delta P_{av} = (1/n)\sum_{i=1}^{n}|P_{expt,i} - P_{calc,i}|$; $\Delta P_{max} = \max |P_{expt,i} - P_{calc,i}|$.

parameters for the modified Margules expression are presented in Table IV, along with the resulting average and maximum deviations in pressure. Pure-component vapor pressures appearing in Table III are not averaged values but are the values obtained for the given run.

The methanol–2-butanol system shows negative deviations from Raoult's law at low methanol concentrations and positive deviations at high methanol concentrations. Vapor–liquid equilibrium measurements have been made at 298.15 K by Polak et al. (*5*). To make a comparison between the two studies, the expression for G^E given by eq 2 with the parameters in Table IV was corrected to 298.15 K by using the heat of mixing data reported by Polak et al. From the pure-component vapor pressures at 298.15 K that Polak et al. report for methanol and 2-butanol, the total pressure was calculated for each of their reported liquid compositions and compared to their measured values. The present study yields pressures that are systematically higher, but the agreement is very good, with an average and maximum deviation of 0.04 and 0.07 kPa, respectively.

At 303.15 K, the *n*-pentane–methanol system is less than 15 K above its upper critical solution temperature (*10*), and consequently, the $P-x$ curve is quite flat. Although an unweighted fit of eq 2 to the data for this system was within experimental error, it yielded an incorrect prediction of liquid–liquid immiscibility. A weighted regression was therefore used for this system in which the objective function (OF) was

$$\mathrm{OF} = \sum_{i=1}^{n}(P_{\mathrm{exp},i} - P_{\mathrm{calc},i})^2/\sigma_{p,i}^{\,2} \tag{5}$$

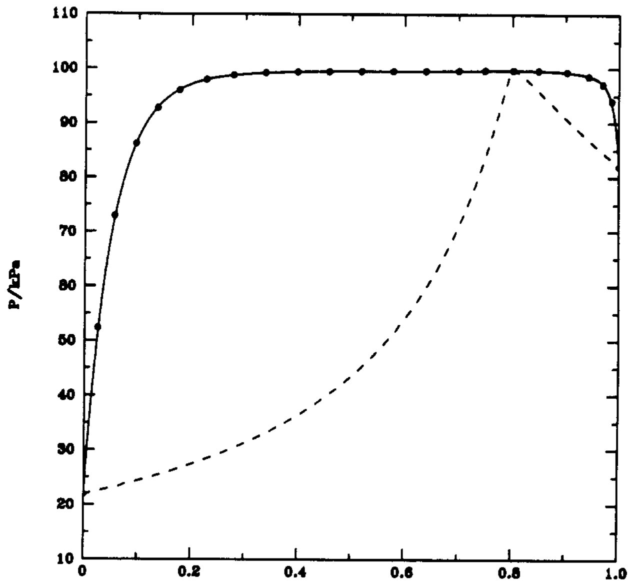

Figure 2. Pressure P vs liquid-phase mole fraction x_1, or vapor-phase mole fraction y_1, for *n*-pentane (1)–methanol (2) at 303.15 K. The points are experimental results, the solid curve is a fitted $P-x$ result, and the dashed curve is a predicted $P-y$ result.

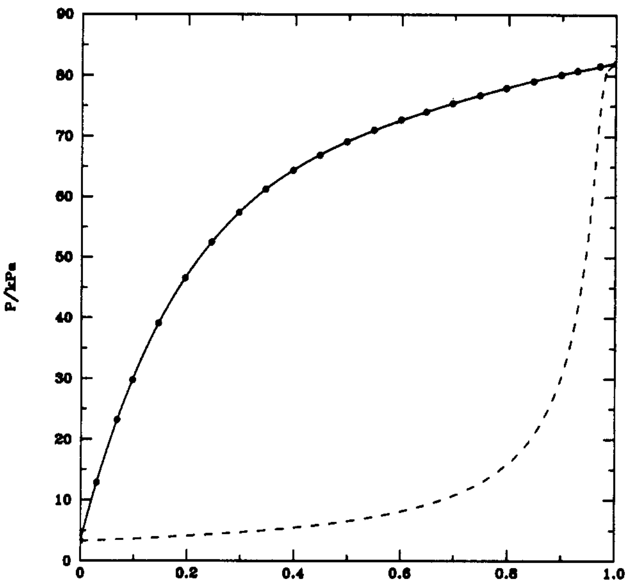

Figure 3. Pressure P vs liquid-phase mole fraction x_1, or vapor-phase mole fraction y_1, for *n*-pentane (1)–2-butanol (3) at 303.15 K. The points are experimental results, the solid curve is a fitted $P-x$ result, and the dashed curve is a predicted $P-y$ result.

where the weighting factor $\sigma_{p,i}$ for each data point i was obtained from

$$\sigma_{p,i} = 0.001P_{\mathrm{exp},i} + 0.001|(\partial P/\partial x_1)_{T,i}| \tag{6}$$

The first term in eq 6 reflects the uncertainty in the measured pressure (0.1% of reading), while the second term reflects uncertainty in the liquid-phase mole fraction (0.001 in mole fraction). While eq 6 should also contain a term reflecting the uncertainty in temperature, not enough information was available to evaluate $(\partial P/\partial T)_x$. However, the inclusion of this term would not substantially affect the results.

The resulting parameters listed in Table IV fit the data to within experimental error and correctly predict miscibility over the entire composition range.

Isothermal vapor–liquid equilibrium measurements for this system have been made at temperatures between 373 and 423

Table V. Total Pressure P for n-Pentane (1)–Methanol (2)–2-Butanol (3) at 303.15 K as a Function of Liquid Mole Fractions x_1 and x_2 for Given Values of the Parameter C', Equation 1

$C' = 0.2459$			$C' = 0.5087$			$C' = 0.7562$		
x_1	x_2	P/kPa	x_1	x_2	P/kPa	x_1	x_2	P/kPa
0.9713	0.0063	85.29	0.9725	0.0130	89.13	0.9721	0.0202	92.97
0.9296	0.0165	85.21	0.9403	0.0293	89.89	0.9420	0.0429	94.38
0.8890	0.0265	84.73	0.8995	0.0500	89.91	0.9013	0.0736	94.83
0.8381	0.0391	83.97	0.8478	0.0764	89.55	0.8501	0.1123	94.85
0.7848	0.0522	83.15	0.7977	0.1019	89.06	0.7984	0.1515	94.63
0.7440	0.0623	82.42	0.7474	0.1276	88.50	0.7473	0.1901	94.38
0.6862	0.0766	81.34	0.6966	0.1535	87.89	0.6969	0.2284	94.03
0.6364	0.0889	80.31	0.6461	0.1792	87.25	0.6457	0.2671	93.70
0.5862	0.1013	79.19	0.5956	0.2050	86.51	0.5953	0.3053	93.31
0.5361	0.1136	77.91	0.5450	0.2308	85.67	0.5450	0.3433	92.87
0.4863	0.1259	76.47	0.4952	0.2562	84.70	0.4944	0.3818	92.34
0.4367	0.1382	74.69	0.4454	0.2816	83.47	0.4445	0.4195	91.67
0.4355	0.1385	74.67	0.3958	0.3069	81.91	0.3947	0.4573	90.77
0.3855	0.1508	72.42	0.3462	0.3322	79.87	0.3448	0.4951	89.53
0.3354	0.1631	69.55	0.3449	0.3327	79.94	0.2955	0.5325	87.78
0.2842	0.1756	65.82	0.2941	0.3585	77.11	0.2463	0.5697	85.17
0.2341	0.1879	60.99	0.2437	0.3841	73.27	0.1971	0.6069	81.22
0.1844	0.2001	54.76	0.1933	0.4096	67.83	0.2441	0.5713	85.03
0.1438	0.2100	48.17	0.1436	0.4349	60.22	0.1936	0.6094	80.86
0.1056	0.2194	40.44	0.0934	0.4604	49.13	0.1437	0.6471	74.27
0.0664	0.2290	30.52	0.0562	0.4792	37.66	0.0941	0.6845	63.59
0.0290	0.2382	18.68	0.0279	0.4936	26.49	0.0557	0.7136	50.49
						0.0273	0.7350	36.34

Table VI. Coefficients in Equations 2 and 4 for the Ternary System n-Pentane (1)–Methanol (2)–2-Butanol (3) at 303.15 K, Average Deviation ΔP_{av}, and Maximum Deviation ΔP_{max}

i,j	A_{ij}	α_{ij}	η_{ij}	C_{ij}
1,2	2.933 64	3.685 82	21.135 23	0.405 96
2,1	4.297 83	21.969 81	21.135 23	0.203 10
1,3	1.486 52	1.544 58	0.935 22	0.513 39
3,1	3.184 89	14.112 39	0.935 22	0.060 51
2,3	−0.141 98	0.181 49		0.100 55
3,2	0.043 58	0.320 26		0.499 32
1,1				0.022 82
2,2				0.223 05
3,3				0.264 44

$C_0 = 7.600\,36$; ΔP_{av}/kPa = 0.09; ΔP_{max}/kPa = 0.28

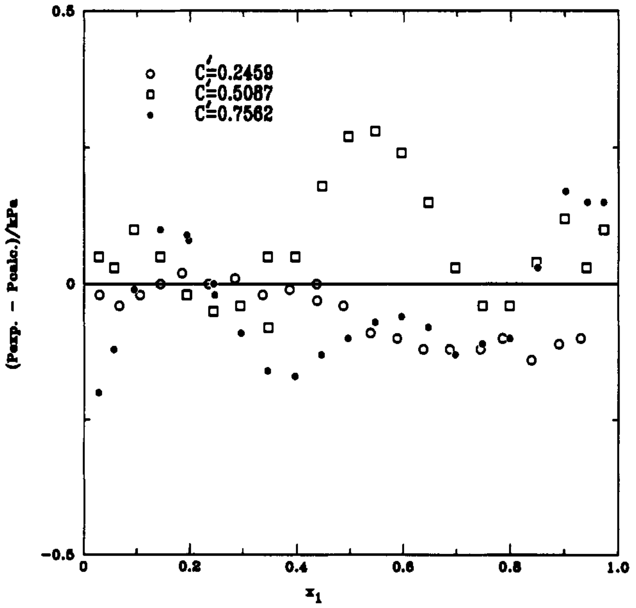

Figure 4. Pressure residuals $P_{expt} - P_{calc}$ for the ternary system n-pentane (1)–methanol (2)–2-butanol (3) at 303.15 K (C' from eq 1).

K by Wilsak et al. (*11*) and isobaric measurements (at 100 kPa) have been reported by Tenn and Missen (*12*). No isothermal data at a temperature close to 303.15 K were located.

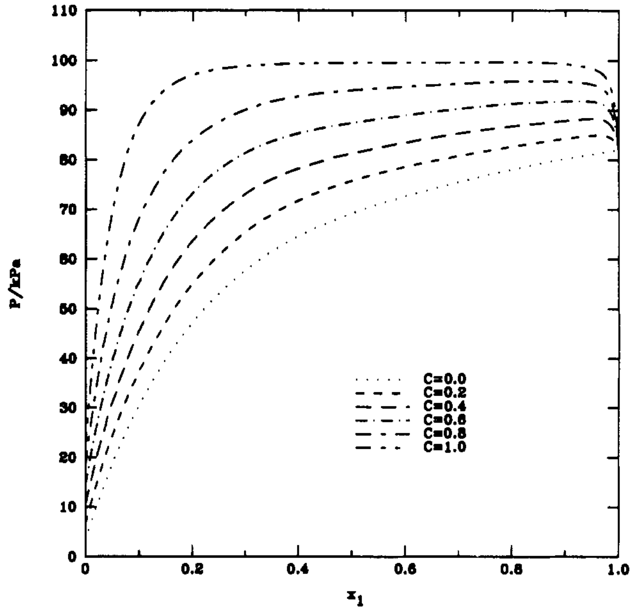

Figure 5. Pressure P vs mole fraction x_1 for n-pentane (1)–methanol (2)–2-butanol (3) at 303.15 K (C from eq 7).

Wilsak et al. presented expressions that relate azeotropic composition and azeotropic pressure to temperature. At 303.15 K, these expressions yield 0.811 and 99.72 kPa respectively for the mole fraction of n-pentane and pressure at the azeotrope. These may be compared to the results of the present study, which yield 0.801 and 99.63 kPa for these quantities.

No literature data for the n-pentane–2-butanol system were located.

The experimental P–x data for the ternary system are presented in Table V.

For the regression of these measurements, the average values of the pure-component vapor pressures were used. With the exception of the n-pentane–methanol run, the binary results presented earlier are based on slightly different vapor pressures. Hence, the methanol-2-butanol and n-pentane–2-butanol binaries were refitted with the average vapor pressures given in Table I. The resulting Margules constants are listed in Table VI. The deviations in pressure for the two refitted

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binary systems were identical with the values given earlier in Table IV.

With use of the binary parameters of Table VI and eqs 3 and 4, the ternary parameters of eq 4 were obtained by Barker's method. These parameter values are given in Table VI. No evidence was found for strong correlation between any of the parameters. The average deviation between calculated, P_{calc}, and measured, P_{expt}, pressures was 0.09 kPa with a maximum deviation of 0.28 kPa. A plot of the pressure residuals, $P_{expt} - P_{calc}$, for the ternary system is given in Figure 4.

On the basis of the parameter values given in Table VI, the $P-x$ surface for the ternary system was calculated and is shown in Figure 5. The parameter C which appears in this figure is defined by

$$C = \frac{x_2}{x_2 + x_3} \tag{7}$$

Glossary

A_{ij}, A_{ji}	binary parameters for G^E, eq 2
B_{ij}	molar second virial coefficient for species i and j, $cm^3\ mol^{-1}$
C	ternary composition parameter, eq 7
C'	ternary composition parameter, eq 1
C_0	ternary parameter for G^E, eq 4
C_{ij}	ternary parameter for G^E, eq 4
F	ternary function for G^E, eq 3
G^E	molar excess Gibbs free energy, $kJ\ mol^{-1}$
P	pressure, kPa
P_i°	vapor pressure of pure species i, kPa
P_{calc}	calculated total pressure, kPa
P_{expt}	measured total pressure, kPa
R	universal gas constant, $kJ\ mol^{-1}\ K^{-1}$
T	temperature, K
V_i^L	saturated molar volume of pure liquid i, $cm^3\ mol^{-1}$
x_i	liquid-phase mole fraction of species i
z_i	overall mole fraction of species i in equilibrium cell

Greek Letters

α_{ij}, α_{ji}	binary parameters for G^E, eq 2
η_{ij}	binary parameter for G^E, eq 2
$\sigma_{p,i}$	weighting factor for ith data point, eq 5, kPa

Registry No. n-Pentane, 109-66-0; methanol, 67-56-1; 2-butanol, 78-92-2.

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Liquid–Liquid Equilibria of the Water + Acetic Acid + Cyclohexyl Acetate Ternary

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Liquid–liquid equilibria for the water + acetic acid + cyclohexyl acetate system were measured at 298.16 ± 0.20, 308.16 ± 0.20, and 318.16 ± 0.20 K. Tie-line compositions were correlated by the reduced Eisen–Joffe equation. Reliability of data was ascertained through Othmer–Tobias plots. Distribution coefficients and separation factors were evaluated over the immiscibility region, and it is concluded that the high-boiling solvent, cyclohexyl acetate, is a suitable separating agent for dilute aqueous acetic acid solutions. In addition, the temperature dependence of solubility and tie-line compositions is insignificant from 298 to 318 K, except at very low acetic acid concentrations.

Introduction

Major advantages of high-boiling separating agents for the extraction of acetic acid from its aqueous solutions have been recently reported (*1–3*). It has also been predicted that cyclohexyl acetate could be used as solvent (*4*).

The objective of this study was to determine the experimental solubility and tie-line compositions of the water + acetic acid + cyclohexyl acetate ternary at 298.16 ± 0.20, 308.16 ± 0.20, and 318.16 ± 0.20 K, at atmospheric pressure. Complete phase diagrams were obtained by evaluating together the solubility and the tie-line compositions for each temperature. In addition, the tie-line compositions were correlated by using the reduced Eisen–Joffe equation (*5*). Their thermodynamic consistency was ascertained by making Othmer–Tobias plots (*6*) and applying an independent material balance check.

In order to determine the most suitable process temperature, free-solvent-based selectivity diagrams at 298.16, 308.16, and

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