210 *J. Chem. Eng. Data* **1995,** *40,* 210–213

Total Pressure Measurements for Chloroform + Acetone + 2-Butanone at 303.15 K

Carlos G. Camero, Venkat R. Bhethanabotla, and Scott W. Campbell*

Department of Chemical Engineering, University of South Florida, Tampa, Florida 33620-5350

Total pressure measurements are reported for chloroform + acetone + 2-butanone, chloroform + 2-butanone, and acetone + 2-butanone at 303.15 K. The results were obtained using a Van Ness apparatus and were fitted to a flexible correlating expression for the excess Gibbs free energy of the liquid phase using Barker's method. This expression represents the measured pressures for the ternary system with an average deviation of 0.03 kPa. The applicability of the NRTL equation to this system is examined, and it is found to predict the ternary results with an average deviation of 0.07 kPa.

Introduction

In a previous publication (*1*) vapor–liquid equilibrium data at 303.15 K for chloroform + acetone + toluene and its constituent binary systems were presented. As a continuation of a study of systems in which dimerization between species occurs, results are presented here for chloroform + acetone + 2-butanone at the same temperature. Since results for chloroform + acetone were reported earlier, only two of the three constituent binaries, chloroform + 2-butanone and acetone + 2-butanone, are examined here.

Vapor–liquid equilibrium data for acetone + 2-butanone at atmospheric pressure have been reported by Babich et al. (*2*), Danciu (*3*), and Othmer et al. (*4*) who also reported measurements at several pressures up to 34.5 bar. In addition, isobaric measurements at 1.0 bar were reported by Yoshikawa and Kato (*5*). Isothermal measurements for a series of temperatures between 293.15 and 323.15 K were reported by Price (*6*).

Isobaric vapor–liquid equilibrium data at atmospheric pressure have been measured for chloroform + 2-butanone by Krishnamurty and Rao (*7*), and isothermal data at 318.15 and 328.15 K have been reported by Ohta et al. (*8*).

No isothermal data for chloroform + acetone + 2-butanone have been located in the literature. However, isobaric data at atmospheric pressure have been reported by Dakshinamurty and Venkata Rao (*9*).

Table 1. Vapor Pressures P_i^{sat}, Saturated Liquid Volumes V_i^L, and Second Virial Coefficients for Single Components B_{ii} and Mixtures B_{ij} Used for Chloroform + Acetone + 2-Butanone at 303.15 K

	chloroform	acetone	2-butanone
P_i^{sat}/kPa	32.395	37.928	15.324
V_i^L/(cm^3 mol^{-1})	81.2	74.5	90.8
B_{ii}/(cm^3 mol^{-1})	−1168	−1835	−2497

Second Virial Cross-Coefficients, B_{ij}/(cm^3 mol^{-1})	
chloroform + acetone	−2330
chloroform + 2-butanone	−2888
acetone + 2-butanone	−2147

Experimental Section

Apparatus and Procedure. The apparatus is identical to that described in detail earlier by Bhethanabotla and Campbell (*10*) except for the replacement of the pressure gauge with one of 0.001 kPa resolution as described by Pradhan et al. (*11*). It is of the Van Ness type (*12*) in which total pressure is measured as a function of overall composition in the equilibrium cell. For binary system measurements, the overall composition in the cell was changed by charging metered amounts of the pure components from their respective piston injectors.

Ternary system measurements were made following the same procedure except that one piston injector contained pure chloroform while the other contained a mixture of acetone + 2-butanone. Hence, a ternary run proceeded along a line of constant mole ratio of acetone to 2-butanone and is characterized by a parameter C', defined as

$$C' = z_2/(z_2 + z_3) \tag{1}$$

where z_2 and z_3 are the overall mole fractions of acetone and 2-butanone, respectively, in the equilibrium cell. Three such runs were made corresponding to C' values of 0.2760, 0.5032, and 0.7341.

The experiment consists of the measurement of the pressure and the overall composition in the equilibrium cell. Corrections to obtain the liquid phase composition are made as part of the data reduction procedure as described earlier (*10*).

Experimental uncertainties are ±0.1% in pressure, ±0.02 K in temperature, and between ±0.0005 and ±0.001 in mole fraction, the smaller value applying at the extremes in composition.

Materials. Chloroform and acetone were obtained as described earlier (*1*) and had purities of 99.9% (by mass) or better. The 2-butanone was obtained from Aldrich Chemical (HPLC grade) and had a purity of 99.5% (by mass) or better. All chemicals were degassed as described by Bhethanabotla and Campbell (*10*). The averages of the pure component vapor pressures measured in this study at 303.15 K are reported in Table 1. The values for chloroform and acetone are 0.086 kPa (0.3%) higher and 0.083 kPa (0.2%) lower than those reported in ref 13. The value for 2-butanone is 0.093 kPa (0.6%) higher than reported by Ambrose et al. (*14*).

Data Reduction. Data were reduced using Barker's method (*15*) and a flexible correlating equation for the excess Gibbs free energy. As before, the binary systems were represented by the four-parameter modified Margules

---

* To whom correspondence should be addressed. e-mail: campbell@sunburn.ec.usf.edu.

0021-9568/95/1740-0210$09.00/0

Table 2. Values of Parameters Appearing in Eqs 2 and 4 and Resulting Average Deviations ΔP_{av} and Maximum Deviations ΔP_{max} for Chloroform + Acetone + 2-Butanone and Its Constituent Binary Systems at 303.15 K

	acetone (i) + 2-butanone (j)	chloroform (i) + 2-butanone (j)	chloroform (i) + acetone (j)
A_{ij}	0.0664	−0.9728	−0.7214
A_{ji}	0.0307	−1.1364	−0.7556
α_{ij}	−0.0467	0.2307	0.4936
α_{ji}	−0.0467	1.2345	3.1276
ΔP_{av}/kPa	0.019	0.043	0.019
ΔP_{max}/kPa	0.065	0.129	0.035

	chloroform (1) + acetone (2) + 2-butanone (3)		chloroform (1) + acetone (2) + 2-butanone (3)
C_{11}	1.3593	C_{13}	−1.0826
C_{22}	−0.1860	C_{23}	0.6359
C_{33}	0.5092	ΔP_{av}/kPa	0.027
C_{12}	−0.5236	ΔP_{max}/kPa	0.140

equation proposed by Abbott and Van Ness (*16*):

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

The ternary results were represented by the form advocated by Abbott et al. (*17*):

$$G^E/RT = (G^E/RT)_{1,2} + (G^E/RT)_{1,3} + (G^E/RT)_{2,3} + F(x_1 x_2 x_3) \quad (3)$$

where the expressions used for $(G^E/RT)_{ij}$ are those obtained from the fits of the modified Margules equation to the three constituent binary systems. The function F was taken to be

$$F = x_1 x_2 x_3 [C_0 - (C_{11} x_1 + C_{12} x_2 + C_{13} x_3) x_1 - (C_{21} x_1 + C_{22} x_2 + C_{23} x_3) x_2 - (C_{31} x_1 + C_{32} x_2 + C_{33} x_3) x_3] \quad (4)$$

where

$$C_{ji} = C_{ij} \quad (5)$$

and

$$C_0 = (1/2) \sum_i \sum_j A_{ij} \qquad i \neq j \quad (6)$$

For a ternary system, eq 4 contains six adjustable parameters. A detailed description of the fitting procedure is given by Bhethanabotla and Campbell (*10*). Second virial coefficients and saturated liquid volumes of the pure chemicals are required for data reduction and are included in Table 1. Second virial coefficients were calculated using the correlation of Tsonopoulos (*18*). It was assumed that $k_{ij} = 0.0$ for acetone + 2-butanone. A value of $k_{ij} = -0.20$ was used for chloroform + acetone and was determined using second virial cross-coefficients measured by Zaalishvili and Kolysko (*19*). It was assumed that k_{ij} for chloroform + 2-butanone was also equal to −0.20. Saturated liquid volumes were taken from ref 13 for chloroform and acetone and from ref 20 for 2-butanone.

Results

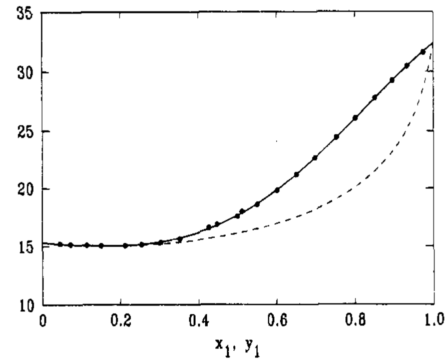

Figure 1. Pressure P vs liquid phase mole fraction x_1 or vapor phase mole fraction y_1 for chloroform (1) + 2-butanone (3) at 303.15 K. The points are experimental results, the solid curve is the fitted $P-x$ result, and the dashed curve is the predicted $P-y$ result.

Table 3. Total Pressure P as a Function of Liquid Phase Mole Fraction x_i for Chloroform (1) + 2-Butanone (3) and Acetone (2) + 2-Butanone (3) at 303.15 K

chloroform (1) + 2-butanone (3)		acetone (2) + 2-butanone (3)	
x_1	P/kPa	x_2	P/kPa
0.0463	15.215	0.0629	16.928
0.0728	15.156	0.1098	18.027
0.1147	15.084	0.1479	18.932
0.1519	15.051	0.1827	19.750
0.2130	15.067	0.2294	20.830
0.2550	15.147	0.2763	21.904
0.3042	15.336	0.3223	22.943
0.3536	15.651	0.3690	23.994
0.4272	16.601	0.4162	25.058
0.4476	16.884	0.4635	26.115
0.5113	17.992	0.5114	27.183
0.4995	17.579	0.5589	28.236
0.5503	18.592	0.6071	29.314
0.6006	19.816	0.5490	27.972
0.6502	21.188	0.5990	29.068
0.6968	22.630	0.6489	30.156
0.7513	24.430	0.6993	31.247
0.8001	26.095	0.7494	32.355
0.8503	27.807	0.7993	33.439
0.8953	29.268	0.8500	34.526
0.9329	30.447	0.8980	35.624
0.9739	31.605	0.9287	36.342
		0.9691	37.209

The results of the data reduction procedure are a set of corrected liquid phase mole fractions for each pressure and values for the parameters appearing in the G^E model. Parameter values and resulting deviations in pressure are given for each system in Table 2. The parameters for chloroform + acetone were obtained by fitting the reuslts of the earlier study (*1*) using the updated value (−0.20) of k_{ij}. The binary data are represented by the G^E model to within an average of 0.04 kPa while the ternary data are represented to within an average of 0.03 kPa.

$P-x$ data at 303.15 K for chloroform + 2-butanone and for acetone + 2-butanone are given in Table 3 and are shown in Figures 1 and 2 where the solid curves represent the fitted $P-x$ result and the dashed curves represent the predicted $P-y$ result. These figures indicate that acetone + 2-butanone shows only slight positive deviations from ideal solution behavior while chloroform + 2-butanone exhibits negative deviations and forms a minimum pressure azeotrope.

Ohta et al. (*8*) measured vapor−liquid equilibrium for chloroform + 2-butanone at 318.15 and 328.15 K and heats of mixing at 308.15 K. A procedure described earlier (*1*), which uses heat of mixing data to compare two sets of vapor−liquid equilibrium data at different temperatures, was applied to compare the results of the present study to those of Ohta et al.

Specifically, the parameters given in Table 2 for chloroform + 2-butanone at 303.15 K (which represent the data of the present study) were combined with the heat of

Table 4. Total Pressure P for Chloroform (1) + Acetone (2) + 2-Butanone (3) at 303.15 K as a Function of Liquid Phase Mole Fractions x_1 and x_2 for Given Values of the Parameter C', Eq 1

$C' = 0.2760$			$C' = 0.5032$			$C' = 0.7341$		
x_1	x_2	P/kPa	x_1	x_2	P/kPa	x_1	x_2	P/kPa
0.0480	0.2617	21.317	0.0456	0.4789	26.291	0.0328	0.7091	31.456
0.0894	0.2503	21.010	0.0884	0.4575	25.786	0.0676	0.6836	30.893
0.1273	0.2399	20.741	0.1268	0.4383	25.339	0.1191	0.6459	30.042
0.1704	0.2281	20.469	0.1633	0.4200	24.922	0.1638	0.6132	29.303
0.2113	0.2169	20.240	0.1948	0.4043	24.565	0.2010	0.5859	28.688
0.2512	0.2060	20.060	0.2616	0.3708	23.878	0.3161	0.5016	26.926
0.3005	0.1925	19.908	0.3011	0.3510	23.529	0.3358	0.4872	26.670
0.3497	0.1790	19.852	0.3507	0.3262	23.171	0.3991	0.4408	25.934
0.3999	0.1652	19.925	0.4002	0.3013	22.930	0.4144	0.4296	25.786
0.4499	0.1515	20.158	0.4502	0.2763	22.837	0.4785	0.3826	25.349
0.4996	0.1379	20.577	0.5002	0.2512	22.923	0.4989	0.3676	25.273
0.5496	0.1241	21.213	0.5000	0.2514	22.879	0.4775	0.3833	25.281
0.5621	0.1040	21.204	0.5501	0.2261	23.150	0.5165	0.3547	25.158
0.6115	0.0922	22.004	0.5996	0.2012	23.643	0.5779	0.3096	25.241
0.6613	0.0804	23.041	0.6366	0.1827	24.167	0.6182	0.2800	25.494
0.7101	0.0688	24.247	0.6995	0.1510	25.303	0.6628	0.2474	25.950
0.7584	0.0574	25.583	0.7490	0.1262	26.380	0.7318	0.1967	26.975
0.8076	0.0457	27.019	0.8002	0.1004	27.622	0.7851	0.1576	27.987
0.8562	0.0341	28.475	0.8399	0.0805	28.615	0.8379	0.1189	29.099
0.9039	0.0228	29.863	0.8991	0.0507	30.070	0.8912	0.0798	30.238
0.9428	0.0136	30.935	0.9408	0.0304	31.023	0.9348	0.0478	31.157
0.9717	0.0067	31.676	0.9694	0.0154	31.689	0.9685	0.0231	31.828

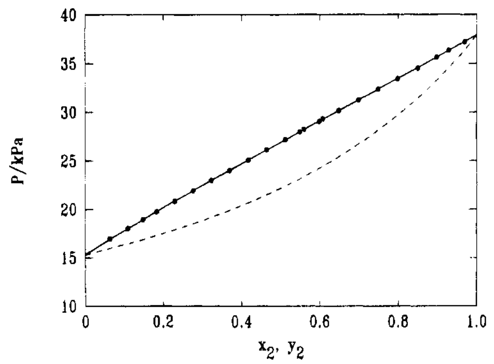

Figure 2. Pressure P vs liquid phase mole fraction x_2 or vapor phase mole fraction y_2, for acetone (2) + 2-butanone (3) at 303.15 K. The points are experimental results, the solid curve is the fitted $P-x$ result, and the dashed curve is the predicted $P-y$ result.

mixing results of Ohta et al. to predict their vapor–liquid equilibrium results at 318.15 K. It was found that the predicted pressures were, on the average, 2.0% higher than those reported by Ohta et al. The predicted vapor phase compositions were different, on average, by 0.006 in mole fraction. These are similar to the deviations that Gmehling et al. (*21*) obtained from a direct fit to the data of Ohta et al. In fact, it is interesting to note that the parameters of the present study predict pressures that are in better agreement (0.6%) with the best fit of Gmehling et al. to the data of Ohta et al. than they are with the data themselves (2.0%).

The temperature range of the available isobaric data for acetone + 2-butanone is too far removed from 303.15 K to make a meaningful comparison with the data reported here. The only isothermal data located for this system are those of Price (*6*) who made measurements at several temperatures including 303.15 K. The pressures reported here are, on the average, 5.3% lower than those of Price. It is believed that the data of Price may be in error since they show a strong positive deviation from ideal solution behavior. The data presented here indicate that acetone + 2-butanone forms a nearly ideal solution. This is in agreement with the heat of mixing results of Ramalho et al. (*22*). Furthermore, the nearly ideal behavior is consistent with the isobaric data.

Table 5. Parameters for the NRTL Equation and Resulting Average Deviations ΔP_{av} and Maximum Deviations ΔP_{max} for Chloroform + Acetone + 2-Butanone and Its Constituent Binary Systems at 303.15 K

	acetone (i) + 2-butanone (j)	chloroform (i) + 2-butanone (j)	chloroform (i) + acetone (j)
τ_{ij}	−0.5175	3.1429	2.6671
τ_{ji}	0.6872	−2.2069	−2.0015
α_{ij}	0.30	0.30	0.30
ΔP_{av}/kPa	0.024	0.042	0.131
ΔP_{max}/kPa	0.076	0.133	0.222

	chloroform (1) + acetone (2) + 2-butanone (3)
ΔP_{av}/kPa	0.071
ΔP_{max}/kPa	0.192

$P-x$ data at 303.15 K for the chloroform + acetone + 2-butanone system are given in Table 4. As in the earlier study (*1*), the ability of a local composition model to describe the ternary data is examined. The NRTL equation (*23*) is considered

$$G^E/RT = \sum_i x_i \left[\sum_j \tau_{ji} G_{ji} \Big/ \sum_k G_{ki} x_k \right] \tag{7}$$

where

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{8}$$

and $\alpha_{ji} = \alpha_{ij}$. The two parameters τ_{ij} and τ_{ji} (α_{ij} was assumed to be 0.3 for all systems) were determined for each binary system using Barker's method, and their values are given in Table 5. These parameters were also used to predict pressures for the ternary liquid compositions and were compared to the experimental results as shown in Table 5. The predictions are excellent and correspond to an average deviation in pressure of 0.071 kPa.

Literature Cited

(1) Hopkins, J. A.; Bhethanabotla, V. R.; Campbell, S. W. *J. Chem. Eng. Data* **1994**, *39*, 488.

(2) Babich, S. V.; Ivanchikova, R. A.; Serafimov, L. A. *Zh. Prikl. Khim.* **1969**, *42*, 1354.

(3) Danciu, E. *St. Cerc. Chim. Tom.* **1968**, *16*, 957.

(4) Othmer, D. F.; Chudgar, M. M.; Levy, S. L. *Ind. Eng. Chem.* **1952**, *44*, 1872.
(5) Yoshikawa, H.; Kato, M. *J. Chem. Eng. Data* **1991**, *36*, 57.
(6) Price, T. W. *J. Chem. Soc.* **1919**, *115*, 1116.
(7) Krishnamurty, V. V. G.; Venkata Rao, C. *J. Sci. Ind. Res.* **1955**, *14B*, 55.
(8) Ohta, T.; Asano, H.; Nagata, I. *Fluid Phase Equilib.* **1980**, *4*, 105.
(9) Dakshinamurty, P.; Venkata Rao, C. *J. Sci. Ind. Res.* **1956**, *15B*, 118.
(10) Bhethanabotla, V. R.; Campbell, S. W. *Fluid Phase Equilib.* **1991**, *62*, 239.
(11) Pradhan, A. G.; Bhethanabotla, V. R.; Campbell, S. W. *Fluid Phase Equilib.* **1993**, *84*, 183.
(12) Gibbs, R. E.; Van Ness, H. C. *Ind. Eng. Chem. Fundam.* **1972**, *11*, 410.
(13) *TRC data bases for Chemistry and Engineering, TRC Thermodynamic Tables*; Thermodynamics Research Center of the Texas Engineering Experiment Station, Texas A&M University System, College Station, TX, 1993.
(14) Ambrose, D.; Ellender, J. H.; Lees, E. B.; Sprake, C. H. S.; Townsend, R. *J. Chem. Thermodyn.* **1975**, *7*, 453.
(15) Barker, J. A. *Aust. J. Chem.* **1953**, *6*, 207.
(16) Abbott, M. M.; Van Ness, H. C. *AIChE J.* **1975**, *21*, 62.
(17) Abbott, M. M.; Floess, J. K.; Walsh, G. E., Jr.; Van Ness, H. C. *AIChE J.* **1975**, *21*, 72.
(18) Tsonopoulos, C. *AIChE J.* **1974**, *20*, 263.
(19) Zaalishvili, Sh. D.; Kolysko, L. E. *Russ. J. Phys. Chem.* **1961**, *35*, 1291.
(20) Malhotra, R.; Woolf, L. A. *J. Chem. Thermodyn.* **1992**, *24*, 1207.
(21) Gmehling, J.; Onken, U.; Rarey, J. R. *Vapor-Liquid Equilibrium Data Collection. Ketones (Supplement 1)*; Chemistry Data Series; DECHEMA: Frankfurt, 1993; Vol. 1., Part 3b.
(22) Ramalho, R. S.; Tillie, J. L.; Kaliaguine, S. *Can. J. Chem. Eng.* **1971**, *49*, 830.
(23) Renon, H.; Prausnitz, J. M. *AIChE J.* **1968**, *14*, 135.

Received for review June 1, 1994. Accepted August 17, 1994.[⊗]

JE940101A

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1994.