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Vapor–Liquid Equilibria for Binary and Ternary Systems Composed of Acetone, 2-Propanol, and 1-Propanol

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The vapor–liquid equilibrium data for the binary and ternary systems composed of acetone, 2-propanol, and 1-propanol at the isobaric condition of 760 mmHg are presented. The experimental data of the binary systems were used to calculate the binary parameters of the Wilson equation. These parameters have been used to calculate vapor-phase compositions and boiling points of related binary and ternary systems. Calculated vapor-phase compositions and boiling points have been obtained very close to the experimental data for each system investigated.

Introduction

The usual technique for obtaining vapor–liquid equilibrium data for binary systems is by direct measurement, i.e., equilibrium is established and phases are sampled and analyzed. However, experimental measurements of vapor–liquid equilibria are quite scarce for ternary or greater component mixtures. The amount of experimental work required to obtain vapor–liquid equilibria for a mixture rises very sharply as the number of components in the mixture increases. Even for a ternary mixture the experimental effort required is almost 1 order of magnitude larger than that needed for a binary mixture. For multicomponent mixtures, it is commonly not economical to make all the measurements necessary for a complete description of desired equilibria of the multicomponent mixture under consideration. They can be calculated from the related binary and pure component data (*1*). This is the best possible estimation of vapor–liquid equilibria for multicomponent mixtures with a minimum of experimental data.

The binary systems of acetone–2-propanol and 2-propanol–1-propanol had been investigated previously (*2*, *3*). In this investigation, the mean deviation between calculated and experimental results were found to be less than the literature values (*4*) for 2-propanol–1-propanol system. The binary system of acetone–1-propanol and the ternary system of acetone–2-propanol–1-propanol have not been investigated previously.

Experimental Section

Purity of Components. The acetone, 2-propanol, and 1-propanol used in this study were pure grade materials obtained from E. Merck Aktiengesellschaft, Darmstadt. The physical constants for the materials appear in Table I.

Procedure. For studies of vapor–liquid equilibrium a variety of apparatuses have been developed (*5*, *6*). Of these, the apparatus developed by the Stansi Educational Division of Fisher Scientific Co., Ltd., Canada (Figure 1), was used in these experiments.

The samples of vapor and liquid phases were analyzed by a gas chromatograph, Perkin-Elmer Model 154-C. As in previous investigations (*7*, *8*) calibration of the column was necessary, because the peak areas and the mole fractions of the components are not directly proportional. To avoid these kind of errors, mixtures with different compositions were prepared and the peak areas of each component were measured. Thus we obtained the peak area–composition data for every system investigated. The vapor–liquid equilibrium compositions at a constant pressure of 760 mmHg were determined from the measurement of the peak areas of each component in the samples and by applying the linear interpolation technique (*9*) to the related peak area–composition data.

Table I. Physical Properties of the Materials

component	bp, K (760 mmHg) lit. (*21*)	bp, K (760 mmHg) measd	refract. index (20 °C) lit. (*21*)	refract. index (20 °C) measd
acetone	329.39	329.45	1.3588	1.3579
2-propanol	355.55	355.65	1.3776	1.3768
1-propanol	370.30	370.30	1.3850	1.3845

Table II. Data of Pure Materials (*1*)

material	T_c, K	P_c, atm	$\mathcal{V}_c$, cm^3 g mol^{-1}	ω	ω_H	μ, D	η
acetone	508.7	46.6	213.5	0.309	0.187	2.88	0.00
2-propanol	508.2	47.6	247.9	0.984	0.201	1.66	0.00
1-propanol	540.7	51.0	220.0	0.612	0.201	1.68	0.57

Table III. Temperature and Molar Liquid Volume of Pure Materials (*1*)

material	T_1, K	$\mathcal{V}_1^L$	T_2, K	$\mathcal{V}_2^L$	T_3, K	$\mathcal{V}_3^L$
acetone	228.15	67.38	273.15	71.48	323.15	76.83
2-propanol	273.15	74.97	323.15	75.06	373.15	83.41
1-propanol	293.15	74.79	343.15	78.96	393.15	84.52

Table IV. Binary Parameters of the Wilson Equation

binary system	$\lambda_{12} - \lambda_{11}$, cal g mol^{-1}	$\lambda_{12} - \lambda_{22}$, cal g mol^{-1}
acetone–2-propanol	205.7209	265.4683
acetone–1-propanol	211.8560	178.8735
2-propanol–1-propanol	−147.5542	289.4333

Table V. Acetone (1)–2-Propanol (2) (at 1 atm)

x	y_{exptl}	Δy	T_{exptl}	ΔT	γ_1	γ_2
0.0828	0.2552	−0.0053	349.86	0.18	1.6826	1.0043
0.0612	0.1990	−0.0048	351.07	0.15	1.7719	1.0023
0.2091	0.4890	−0.0035	344.14	0.21	1.4814	1.0279
0.1959	0.4703	−0.0038	344.65	0.22	1.5002	1.0244
0.2710	0.5650	−0.0018	342.00	0.18	1.3995	1.0475
0.2601	0.5529	−0.0021	342.35	0.18	1.4131	1.0436
0.3755	0.6612	0.0005	339.06	0.12	1.2833	1.0935
0.4874	0.7375	0.0018	336.57	0.06	1.1856	1.1634
0.4812	0.7337	0.0017	336.70	0.06	1.1903	1.1589
0.5427	0.7691	0.0021	335.52	0.04	1.1462	1.2070
0.5377	0.7663	0.0020	335.61	0.04	1.1495	1.2028
0.5712	0.7843	0.0021	335.01	0.02	1.1280	1.2321
0.5722	0.7849	0.0021	335.00	0.03	1.1274	1.2330

$S_y = 0.0013$
$S_T = 0.0721$

Binary Data

The experimental results of the binary system under consideration and related pure component data (Tables II and III) were used to calculate the binary parameters of the Wilson equation (*10*) by using the simplex search method (*11*) pres-

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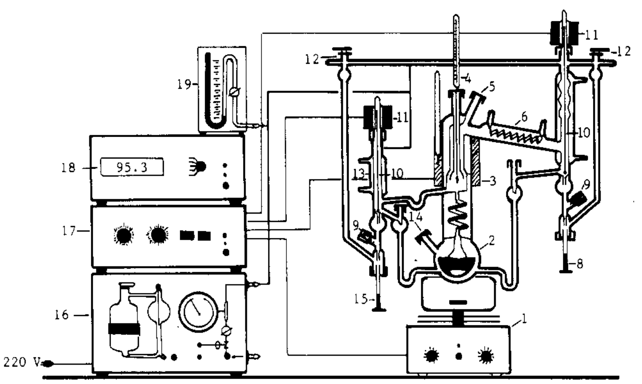

Figure 1. Apparatus. 1, heater; 2, flask; 3, jacketed heater; 4, thermometer; 5, screwed cover; 6, condenser; 7, screwed cover; 8, discharge valve of vapor phase; 9, valves; 10, magnetic valves; 11, bobbins; 12, three-way valves; 13, condenser; 14, screwed cover; 15, discharge valve of liquid phase; 16, adjusting equipment of vacuum; 17, adjustment of heat; 18, digital thermometer; 19, vacuum meter.

Table VI. Acetone (1)-1-Propanol (2) (at 1 atm)

x	y_{exptl}	Δy	T_{exptl}	ΔT	γ_1	γ_2
0.1080	0.4031	0.0028	359.70	-0.06	1.5050	1.0063
0.2417	0.6336	-0.0032	351.50	0.42	1.3485	1.0321
0.3555	0.7432	-0.0023	345.80	-0.09	1.2431	1.0708
0.4742	0.8176	-0.0016	341.65	-0.07	1.1570	1.1296
0.6074	0.8774	-0.0005	338.15	0.21	1.0855	1.2213
0.7129	0.9151	0.0000	336.00	0.67	1.0452	1.3178

$S_y = 0.0012$
$S_T = 0.2239$

Table VII. 2-Propanol (1)-1-Propanol (2) (at 1 atm)

x	y_{exptl}	Δy	T_{exptl}	ΔT	γ_1	γ_2
0.1928	0.3168	0.0006	365.65	-0.02	1.0964	1.0038
0.3078	0.4583	0.0004	363.46	-0.02	1.0749	1.0104
0.3773	0.5320	0.0003	362.28	-0.23	1.0629	1.0163
0.4217	0.5753	0.0003	361.58	-0.03	1.0558	1.0209
0.4724	0.6217	0.0002	360.82	-0.03	1.0476	1.0272
0.5713	0.7044	0.0000	359.47	-0.03	1.0333	1.0426
0.6492	0.7638	-0.0002	358.51	-0.02	1.0234	1.0584
0.6861	0.7905	-0.0003	358.08	-0.02	1.0192	1.0672

$S_y = 0.0002$ $\quad$ $\text{MD}_y = 0.0002$ $\quad$ $\text{MD}_y = 0.0198$ (*4*)
$S_T = 0.0618$

Table VIII. Consistency Test

	ratio of areas	
	this work	ref *2*
acetone-2-propanol	1.004	1.011
acetone-1-propanol	1.005	
2-propanol-1-propanol	1.002	

ented in Table IV. Then, the vapor-phase composition and the boiling points of the mixtures were calculated by using these parameters at the same pressure and liquid-phase compositions. The root-mean-square deviations between experimental and calculated vapor-phase compositions and the measured and calculated boiling points for each system are given in Tables V-VII.

The results of applying the area consistency test of Herington (*12*) and Redlich and Kister (*13*) are summarized in Table VIII. In general, the limits for the ratio of areas above and below the log $(\gamma_1/\gamma_2) = 0$ line proposed by Ellis and Bourne (*14*) at 0.95-1.05 for consistent data are satisfied.

The activity coefficients of the liquid phase were calculated by using the Wilson equation (*10*) for each system. For accurate prediction of vapor-liquid equilibria, it is usually necessary to take vapor-phase nonideality into account. This may be done through the use of an equation of state as discussed in numerous references (*15*, *16*). In this investigation, the correction of vapor-phase nonideality was made by using the fugacity coefficient of each component in the mixture. For this purpose, the virial equation of state (*16*) was used. The second virial coefficients were calculated from the correlation based on an extended corresponding theory developed by O'Connell and Prausnitz (*17*).

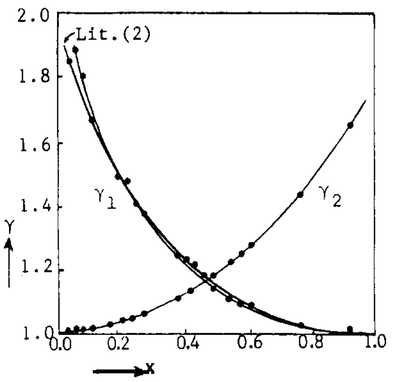

Figure 2. Activity coefficient-composition diagram for acetone (1)-2-propanol (2) system.

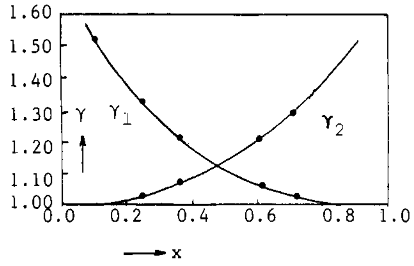

Figure 3. Activity coefficient-composition diagram for acetone (1)-1-propanol (2) system.

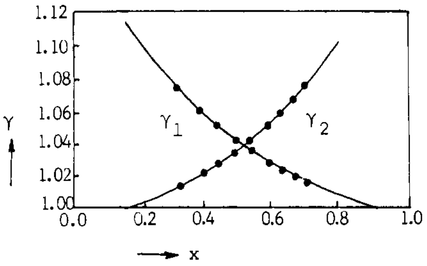

Figure 4. Activity coefficient-composition diagram for 2-propanol (1)-1-propanol (2) system.

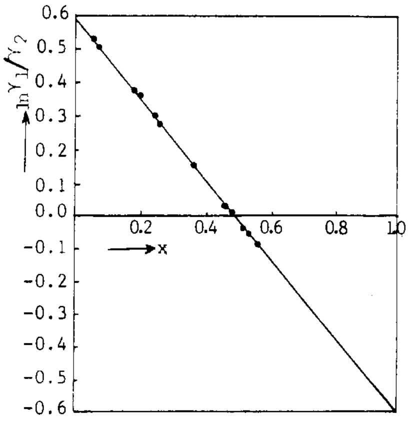

Figure 5. Area test for acetone (1)-2-propanol (2) system.

The experimental and calculated data for the three binary systems are reported in Tables V-VII. The liquid-phase activity coefficients vs liquid-phase compositions in Figures 2-4 and log (γ_1/γ_2) vs liquid-phase compositions are shown in Figures 5-7.

Table IX. Acetone (1)-2-Propanol (2)-1-Propanol (3) (at 1 atm)

x_1	x_2	$y_{1,\mathrm{exptl}}$	$y_{2,\mathrm{exptl}}$	Δy_1	Δy_2	T_{exptl}	ΔT	γ_1	γ_2	γ_3
0.6525	0.1373	0.8487	0.0765	-0.0123	-0.0024	336.42	0.94	1.0690	1.3657	1.2630
0.5295	0.1149	0.8177	0.0687	0.0003	-0.0033	339.65	0.76	1.1252	1.2688	1.1672
0.4536	0.2255	0.7556	0.1389	-0.0014	-0.0021	340.96	0.90	1.1745	1.1977	1.1275
0.3676	0.3897	0.6705	0.2476	-0.0064	0.0047	342.12	0.79	1.2483	1.1258	1.1024
0.2744	0.5262	0.5804	0.3486	-0.0015	0.0027	343.70	0.14	1.3464	1.0723	1.0886
0.2121	0.6069	0.5113	0.4172	0.0080	-0.0080	344.98	-0.54	1.4236	1.0465	1.0866
0.1923	0.5219	0.4926	0.3875	0.0104	-0.0106	346.50	-0.81	1.4289	1.0539	1.0627
0.1355	0.6462	0.3923	0.5087	0.0129	-0.0117	347.93	-1.16	1.5187	1.0295	1.0767
0.1216	0.7117	0.3704	0.5572	0.0209	-0.0151	348.29	-0.95	1.5529	1.0210	1.0921
0.0850	0.7932	0.2912	0.6479	0.0251	-0.0240	349.78	-0.92	1.6255	1.0109	1.1119
0.0619	0.8448	0.2302	0.7214	0.0247	-0.0228	350.67	-1.07	1.6759	1.0061	1.1273

$S_{y_1} = 0.0086$ $S_{y_2} = 0.0076$ $S_{y_3} = 0.0040$ $S_T = 0.2648$

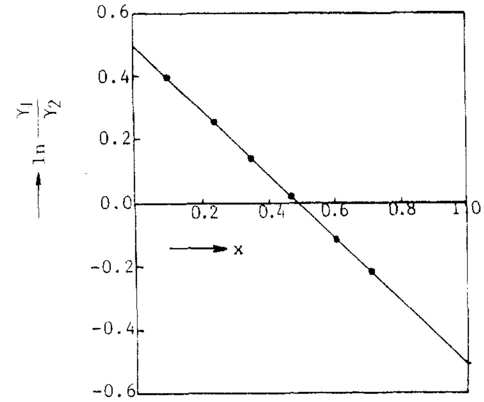

Figure 6. Area test for acetone (1)-1-propanol (2) system.

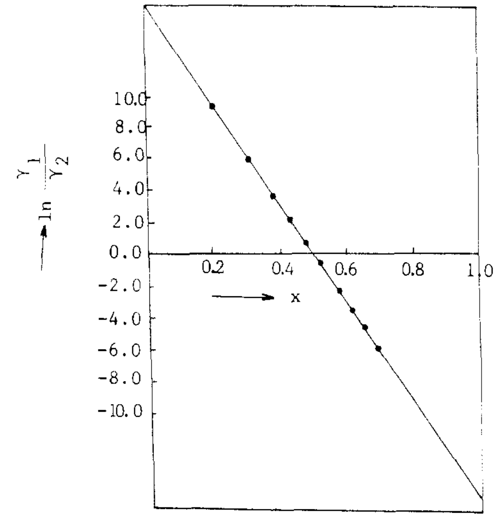

Figure 7. Area test for 2-propanol (1)-1-propanol (2) system.

Ternary Data

The ternary system acetone-2-propanol-1-propanol has not been investigated previously. To obtain vapor-liquid equilibrium data for ternary or greater component mixtures for all possible combinations of compositions would require a lot of experimental measurements. In this investigation, the experimental vapor-liquid equilibrium data were obtained for several different compositions (Table IX). On the other hand, the vapor-liquid equilibrium data were calculated by using related binary parameters. The experimental and calculated data were found to be very close to each other for the vapor phase and boiling points. The root-mean-square deviations between calculated and experimental results are shown in Table IX. The comparison with experimental results indicates that the calculations show good agreement with data for this ternary system of acetone-2-propanol-1-propanol. After that we can predict the vapor-phase compositions and boiling points of liquid-phase composition of the mixture at the same pressure.

Table X. Constants of the Vapor Pressure Equation[a]

$$\ln P = C_1 + C_2/T + C_3T + C_4 \ln T$$

material	C_1	C_2	C_3	C_4
acetone	127.130346	-7314.733098	0.026934	-19.631473
2-propanol	231.069494	-11321.845381	0.057795	-37.416913
1-propanol	-21.070007	-5197.246870	-0.018187	7.070192

[a] P, vapor pressure (atm); T, boiling point (K).

Vapor Pressures

The vapor pressures of the three components have been reported extensively in literature for the temperature range required (*18*). An equation was needed that described the variation in vapor pressure with temperature for use in the digital computer programs written for the treatment of experimental results. The type of equation proposed by Riedel (*19*) was used. The constants of the modified Riedel equation were determined previously by Gültekin (*20*) for more than 1000 substances. These constants are shown in Table X for acetone, 2-propanol, and 1-propanol.

Discussion

The Wilson equation was found to be applicable to the binary and ternary mixtures of which the vapor-liquid equilibria were investigated here. The vapor-phase compositions and boiling points were calculated from system pressure and liquid-phase composition data. The calculated and experimental data for all of the systems were found to be very close to each other.

If the vapor-liquid equilibrium data of the ternary mixtures under consideration are needed, they can be calculated from the related binary Wilson parameters without any additional assumptions.

Glossary

C_1, C_2, C_3, C_4	constants of the vapor pressure equation
MD	mean deviation
P	pressure
S	standard deviation
T	temperature
$\mathcal{V}$	molar volume
x	liquid-phase mole fraction
y	vapor-phase mole fraction
Δy	difference between experimental and calculated vapor-phase compositions
ΔT	difference between experimental and calculated boiling points of the mixtures

Greek Letters

γ	activity coefficient
λ	interaction parameter

μ	dipole moment
η	association factor
ω	acentric factor

Subscripts

c	critical constant
exptl	experimental
H	homomorph compound
L	liquid phase
T	temperature
V	vapor phase

Registry No. Me_2CO, 67-64-1; 2-PrOH, 67-63-0; PrOH, 71-23-8.

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Simple Apparatus for Vapor–Liquid Equilibrium Measurements with Data for the Binary Systems of Carbon Dioxide with *n*-Butane and Isobutane

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We describe the design, construction, and testing of a simple vapor–liquid equilibrium apparatus designed for measurements in the range 300–500 K at pressures to 150 bar. Data are given for measurements of P, T, x, and y for binary systems of carbon dioxide with *n*-butane and isobutane in the range 310–394 K.

Introduction

This apparatus was designed to fill the need for measurements in the temperature range of 300–500 K, which is important both industrially and theoretically and includes the supercritical region of carbon dioxide. It complements an earlier cryogenic apparatus in our laboratory and is similar in principle to a number of existing devices, with, however, one or two novel differences. It satisfies our criteria for an apparatus that is simple in design, easy to build using mostly commercially available components, and capable of efficient acquisition of accurate data.

In the next section we give details of the design and construction of the apparatus and also estimates and results of tests of the accuracy of the various measured quantities. Following that we present data for the systems CO_2 + *n*-butane and CO_2 + isobutane in the range from 310 to 394 K. These data represent a continuation of our earlier work on these systems (*1*), where we have made measurements from 250 to 280 K. That earlier work was performed with the cryogenic apparatus.

In this temperature range several studies have previously been made on the CO_2 + *n*-butane system: Besserer and Robinson (*2*) and Behrens and Sandler (*3*) at 310.9 K, Poettman and Katz (*4*), 305–415 K, Olds et al. (*5*), 311–411 K, and Hsu, Nagarajan, and Robinson (*6*), 319–378 K. For the system with isobutane Besserer and Robinson (*7*) measured isotherms in the range 311–394 K. A recent publication by Leu and Robinson (*8*) gives data for CO_2 with both *n*-butane and isobutane in the range 368–418 K. Some of our data were measured at the same temperatures as these references, and comparisons are made where the isotherms coincide.

Apparatus

The apparatus is shown schematically in Figure 1. It is a vapor and liquid recirculation type. Central to the design is a commercial, top-loading convection oven. The oven is lighted and is equipped with a three-layer glass window for visual observations. In place of the hinged lid, we substituted a lift-off top constructed from 1-in.-thick closed-cell foam, faced with aluminum foil and sandwiched between two layers of 0.5-in. plywood. All of the apparatus is either mounted on top of this lid or suspended from the underside to facilitate adjustments and modifications. The oven temperature is controlled by means of a solid-state device that utilizes a J-type thermocouple for a sensor and has a 4–20-mA output to a proportioning SCR power controller that drives the 3-kW heater. A large fan provides vigorous convection, and we have added some baffles

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† Formerly National Bureau of Standards.