Isobaric Vapor-Liquid Equilibria for Three Binary and Two Ternary Systems

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Vapor-liquid equilibrium data were determined in a Jones vapor-recirculating still for three binary systems, at 500 mm Hg, and two ternary systems, at atmospheric pressure. Among the binary systems, carbon tetrachloride–2-propanol showed a minimum boiling azeotrope at 0.708 mole fraction of carbon tetrachloride and 57.7° C; methyl acetate–methanol formed a minimum boiling azeotrope at 0.698 mole fraction of methyl acetate and 42.9° C; and methyl acetate–ethanol was a nonazeotropic system. The two ternary systems investigated are carbon tetrachloride–cyclohexane–benzene and methyl acetate–methanol–benzene. The data were analyzed and correlated with the Wilson and NRTL equations.

Vapor-liquid equilibrium data were obtained to test the workability of the recently published predicative methods for nonideal systems.

EXPERIMENTAL

Materials. All chemicals except cyclohexane were of chemically pure grade. Cyclohexane of a guaranteed purity was used without further purification. Benzene was subjected to repeated recrystallization. Methanol and ethanol were fractionated in a glass column packed with McMahon packings. 2-Propanol was redistilled in the same column after storage over copper anhydride. Carbon tetrachloride was treated with three successive portions of 100 ml of alcoholic sodium hydroxide, then the carbon disulfide-free solvent was washed several times with water, dried, and distilled. The distillate was shaken with 20 grams of anhydrous potassium carbonate and redistilled. Table I shows a comparison of the physical properties of these materials with the literature values.

Procedure. The still used to obtain vapor-liquid equilibrium data is a Jones still (*4*). The pressure in the equilibrium chamber was maintained at 500 mm Hg by using a Cartesian manostat. The pressure was indicated by means of a mercury manometer and the height of the mercury legs was measured by a cathetometer. The atmospheric pressure was observed during each experimental run and necessary corrections were made (*4*). The equilibrium temperature was measured with copper-constantan thermocouples, which were calibrated against a standard mercury thermometer calibrated by the National Research Laboratory of Metrology. Vapor and liquid samples were analyzed using density and/or refractive index measurements at 25° ± 0.1° C. An Ostwald pycnometer, a Shimadzu balance, and a Shimadzu Pulfrich refractometer were used for these purposes. The accuracy of the measurements was within ±0.0001 of observed values. The uncertainty involved in the experimental values was considered as follows: composition, 0.001 mole fraction; pressure, ±0.1 mm Hg; temperature, ±0.1° C.

EXPERIMENTAL RESULTS AND CORRELATION OF DATA

An equilibrium equation combining the vapor phase composition and the liquid phase composition by considering nonideality in both phases may be expressed as

$$\psi_i y_i P = \psi_i^s x_i \gamma_i P_i^s \exp\left[v_i(P - P_i^s)/RT\right] \tag{1}$$

where it is assumed that the partial molar volume of component *i* is equal to the saturated molar volume of pure liquid *i* at the solution temperature, and that the molar volume is not a function of pressure for subcritical components. The fugacity coefficient is approximately given by the virial equation truncated after the second virial coefficient term (*7, 14*). Second virial coefficients for pure gases and cross coefficients were calculated by empirical methods (*12, 14*). The vapor pressures of the pure components were obtained from the literature (*1, 10, 14*). The liquid phase activity coefficients were correlated with the Wilson and nonrandom, two-liquid (NRTL) equations (*14, 15*).

Binary Systems. Experimental data are deposited with the ASIS (*22*). Azeotropic compositions and temperatures

Table I. Physical Properties of Compounds

Compound	Bp, ° C	Density, 25° C	Refractive index n_D, 25° C
Methyl acetate	56.8	0.9273	1.3588
	56.9 (*19*)	0.9279 (*19*)	1.3589 (*8*)
Methanol	64.7	0.7867	1.3263
	64.65 (*19*)	0.78653 (*19*)	1.32663 (*21*)
Carbon tetrachloride	76.8	1.5844	1.4575
	76.75 (*21*)	1.5842 (*21*)	1.45759 (*21*)
Ethanol	78.3	0.7852	1.3595
	78.3 (*19*)	0.7851 (*19*)	1.35929 (*19*)
Benzene	80.1	0.8735	1.4979
	80.1 (*19*)	0.87364 (*19*)	1.49792 (*19*)
Cyclohexane	80.8	0.7739	1.4236
	80.72 (*19*)	0.7737 (*19*)	1.42354 (*21*)
2-Propanol	82.3	0.7807	1.3747
	82.4 (*21*)	0.78083 (*21*)	1.3747 (*21*)

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Table II. Parameters of Wilson and NRTL Equations and Root-Mean-Square Deviations for Binary Data

System Component 1	 Component 2	Mm Hg	Parameters (cal/mol) Wilson, $(g_{12} - g_{22})$ $(g_{21} - g_{11})$	 NRTL, $(g_{12} - g_{22})$ $(g_{21} - g_{11})$	α_{12}	Deviation in vapor mole fraction × 1000 Wilson	 NRTL	Relative deviation in pressure × 1000 Wilson	 NRTL	Data source
Benzene		760	135	245	0.30	2	2	2	3	(9)
	Cyclohexane		149	26						
Carbon tetrachloride		760	400	472	0.30	4	4	5	5	(3)
	Benzene		−250	−308						
Carbon tetrachloride		760	70	66	0.30	5	5	5	5	(17)
	Cyclohexane		40	37						
Carbon tetrachloride		500	1300	1000	0.47	7	8	6	7	This work
	2-Propanol		106	320						
Methanol		760	100	668	0.47	9	9	12	8	(10)
	Benzene		1740	1126						
Methyl acetate		760	−320	−137	0.30	8	10	9	5	(8)
	Benzene		670	387						
Methyl acetate		500	495	282	0.30	6	6	4	3	This work
	Ethanol		148	325						
Methyl acetate		500	790	346	0.30	5	5	4	3	This work
	Methanol		−75	322						
		760	761	296	0.30	7	7	6	6	(10)
			−73	352						

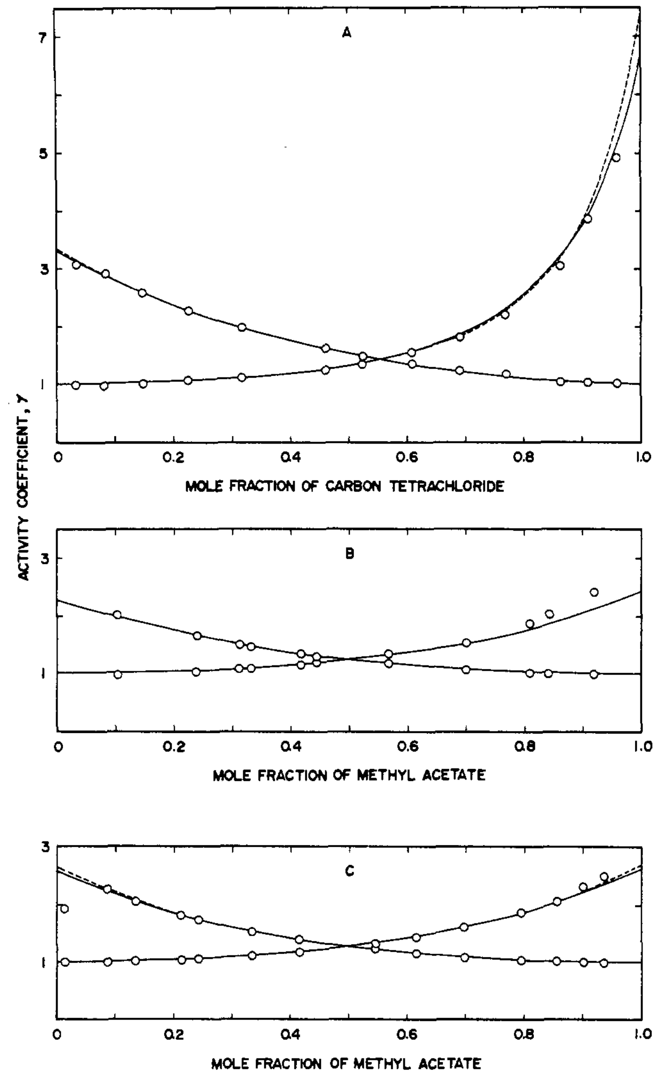

Figure 1. Activity coefficient vs. composition diagrams

A.	Carbon tetrachloride–2-propanol	0.	Experimental
B.	Methyl acetate–ethanol	----	Wilson eq.
C.	Methyl acetate–methanol	—	NRTL eq.

interpolated from smoothed experimental values are:

System	x_1	t, °C
Carbon tetrachloride(1)-2-propanol(2)	0.708	57.7
Methyl acetate(1)-methanol(2)	0.698	42.9

The area test proposed by Herington (4) was used to check the thermodynamic consistency of the data.

System	D	J
Carbon tetrachloride–2-propanol	4.4	6.6
Methyl acetate–ethanol	7.9	10.7
Methyl acetate–methanol	1.4	5.4

Herington proved thermodynamically that if the condition $D < J$ is fulfilled, it can be assumed that the measured data are consistent. This test is applicable to mixtures not far from room temperature.

$$D = \left| \frac{\text{Area above } x\text{-axis} - \text{area below } x\text{-axis}}{\text{Area above } x\text{-axis} + \text{area below } x\text{-axis}} \right| \times 100 \qquad (2)$$

It can be seen that $D < J$ for all systems. The activity coefficients observed at isobaric condition must be corrected to a specific temperature (20), because the area test is valid only for isothermal conditions. The excess enthalpy data for methyl acetate–alcohol systems are available at 25°, 35°, and 45° C (11, 18). For the methyl acetate–ethanol system, D is 0.1 at 50° C; for the methyl acetate–methanol system, D is 0.4 at 45° C. These small values of D suggest that the data are consistent (13). Experimental data for methyl acetate–methanol at 39.76° and 49.76° C were reported by Bredig and Bayer (2). Their data obtained by using the differential distillation technique cannot be as accurate compared with the current data corrected to 45° C.

The numerical values of the Wilson and NRTL parameters for binary systems are listed in Table II with the root-mean-square deviation of calculated from experimental vapor compositions and the root-mean-square relative deviation of calculated from experimental pressures. The parameters were determined by minimizing the sum of these deviations. The deviations for eight systems are nearly equivalent to the results obtained by Renon (15) for 60 binary systems. The Wilson and NRTL equations give similar results for the activity coefficient vs. liquid mole fraction (Figure 1).

Table III. Comparison of Prediction of Ternary Vapor-Liquid Equilibria with Wilson and NRTL Equations

System	No of data points	Deviation in vapor mole fraction^a × 1000				Relative deviation in pressure^b × 1000				Absolute deviation in pressure^c, mm Hg			
		A^d		R^e		A^d		R^e		A^d		R^e	
		Wilson	NRTL	Wilson	NRTL	Wilson	NRTL	Wilson	NRTL	Wilson	NRTL	Wilson	NRTL
Cyclohexane		0	0	5	4								
Carbon tetrachloride	29	1	1	4	4	3	1	5	5	2	1	4	4
Benzene		−1	−1	4	4								
Methyl acetate		1	2	5	5								
Methanol	18	2	2	5	6	3	1	8	7	−2	−1	6	6
Benzene		−3	−4	4	5								

^{a} $\Delta y = y_{\text{calcd}} - y_{\text{exptl}}$. ^{b} $\Delta P_{\text{rel}} = (P_{\text{calcd}} - P_{\text{exptl}})/P_{\text{exptl}}$. ^{c} $\Delta P_{\text{abs}} = P_{\text{calcd}} - P_{\text{exptl}}$. ^{d} A = Arithmetic. ^{e} R = Root mean square.

Ternary Systems. Experimental data are deposited with the ASIS (*22*). Calculated results at the temperatures corrected to 760 mm Hg are also deposited with the ASIS (*22*). Table III shows the magnitude of the deviations of the calculated values from the experimental results at the boiling temperatures corrected to 760 mm Hg. A survey of this table indicates that good agreement is obtained between the calculated and the observed values. To indicate the utility of the Wilson equation, Holmes and Van Winkle (*5*) presented the arithmetic absolute deviations in the vapor mole fraction and boiling temperatures for 15 ternary systems, Hudson and Van Winkle (*6*), for 30 ternary systems. These investigators assumed vapor-phase ideality in their calculations. Renon and Prausnitz (*16*) compared the mean arithmetic deviations in the vapor mole fractions and the mean relative deviations in pressures for 12 ternary systems using the Wilson and NRTL equations with the assumption of vapor-phase nonideality. Comparison of the present results and those obtained by these three investigations shows that the prediction accuracy of the Wilson and NRTL equations obtained for the current ternary systems is significantly good and the data should be consistent.

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NOMENCLATURE

D = constant, Equation 2
g_{ij} = interaction energy of i-j pair, cal/g mol
J = $150|\theta|/T_{\min}$
P = total pressure, atm
P_i^s = saturation pressure of pure component i, atm
R = gas constant, 1.987 cal/g mol, °K
T = absolute temperature, °K
$T_{\min}$ = lowest measured boiling temperature, °K
x_i = liquid phase mole fraction of component i
y_i = vapor phase mole fraction of component i
v_i = liquid molar volume of pure component i, cc

Greek Letters

α_{12} = nonrandomness constant for binary 1-2 interaction
ϕ_i = fugacity coefficient of component i
ϕ_i^s = fugacity coefficient of pure component i
γ_i = liquid phase activity coefficient of component i
θ = overall range of boiling points of system, °C

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