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Binary Vapor–Liquid Equilibria of Iso Alcohol–Tetrachloroethene Systems

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Vapor–liquid equilibrium data for two binary iso alcohol–tetrachloroethene systems are measured at 760 mmHg pressure. these two systems are nonideal in behavior and show positive deviations from Raoult's law. The data are correlated by the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations.

In order to develop predictive methods for vapor–liquid equilibria, a continuing study on various binary systems is in progress at this laboratory. As part of this, two binary systems comprising either 2-methyl-1-propanol or 3-methyl-1-butanol in a common solvent, tetrachloroethene, were studied at 760 ± 1 mmHg pressure.

Experimental Section

Purity of Chemicals. The iso alcohols and tetrachloroethene were of reagent grade and were further purified in a laboratory-packed distillation column. The physical properties of these chemicals are presented in Table I. These values compare well with the literature values (*16*).

Equilibrium Still and Analytical Method. An equilibrium still of Jones, Schoenborn, and Colburn as modified by Ward (*15*) was used for the determination of the vapor–liquid equilibria. The details of the still and its operation were described elsewhere (*11*). Equilibrium in the still was attained in 45–60 min depending on the temperature range of the binary mixture. Equilibrium was assumed to be attained when the boiling temperature was constant. In all of the runs, the still was allowed to operate for an additional 60–90 min after getting the equilibrium temperature to ensure complete attainment of equilibrium.

The equilibrium vapor and liquid samples were analyzed by refractive index. For this purpose, mixtures of known composition were prepared at intervals of ~10 mol %, and their refractive indexes were measured. The refractive index vs. composition data for the two binary mixtures are given in Table II. A standard calibration chart of the refractive index vs. composition was prepared for each system on 75 × 50 cm graph paper. Refractive-index measurements were taken at 30 °C for sodium light by using an Abbe's precision refractometer which gave direct readings to three significant figures and had an accuracy to the nearst 0.0005. This corresponds to a maximum error of 0.0055 mole fraction. The equilibrium temperature was measured by a standard mercury in glass thermometer having an accuracy of 0.1 °C.

Table I. Physical Properties of Chemicals

compd	normal bp, °C exptl	normal bp, °C lit.[13]	refractive index at 30 °C exptl	refractive index at 30 °C lit.[13]
2-methyl-1-propanol	107.9	107.89	1.3920	1.391 63
3-methyl-1-butanol	131.7	132.0	1.4035	1.402 84
tetrachloroethene	121.3	121.20	1.5019	1.5018

Table II. Refractive Index vs. Composition Data

2-Methyl-1-propanol (1)–Tetrachloroethene (2)

mole fraction of 2-methyl-1-propanol	refractive index	mole fraction of 2-methyl-1-propanol	refractive index
0.0000	1.5019	0.6261	1.4339
0.1071	1.4889	0.7000	1.4230
0.2191	1.4769	0.8000	1.4129
0.3252	1.4662	0.9000	1.4025
0.4305	1.4540	1.0000	1.3920
0.5259	1.4442		

Tetrachloroethene (1)–3-Methyl-1-butanol (2)

mole fraction of tetrachloroethene	refractive index	mole fraction of tetrachloroethene	refractive index
0.0000	1.4035	0.6142	1.4619
0.1062	1.4142	0.7055	1.4710
0.2096	1.4232	0.7854	1.4810
0.3130	1.4327	0.9131	1.4913
0.4130	1.4424	1.0000	1.5019
0.5111	1.4519		

Table III. Antoine Constants and Constants for Molar Volumes

constant	2-methyl-1-propanol	3-methyl-1-butanol	tetrachloroethene
A	8.53516	7.38170	7.62930
B	1950.940	1373.780	1803.96
C	237.147	174.333	258.976
a	90.56	106.92	85.75
b	0.07237	0.1006	0.0853
c	0.409×10^{-3}	0.0	0.889×10^{-4}

Results and Discussion

The liquid-phase activity coefficient of a component in a highly nonideal mixture is related to the liquid- and vapor-phase mole fractions of the component at equilibrium conditions as follows:

$$\gamma_i = \frac{\phi_i \pi y_i}{x_i \phi_i^s P_i^0 \exp[\bar{V}_i^L(\pi - P_i^0)/(RT)]} \tag{1}$$

Table IV. Effect of Vapor-Phase Nonideality on Liquid-Phase Activity Coefficients of 2-Methyl-1-propanol at 760 ± 1 mmHg

temp, °C	ϕ (eq 3)	% deviation in γ-value with vapor-phase nonideality correction
114.9	0.011530	1.070
111.9	0.006677	0.570
111.3	0.005683	0.496
109.1	0.001998	0.180
108.5	0.000099	0.007
107.9	0.000000	0.000
107.0	−0.001100	0.110
108.1	0.000000	0.000
106.4	−0.002000	0.220
104.0	−0.006010	0.600
103.5	−0.007020	0.710
103.2	−0.007020	0.710
102.9	−0.008030	0.786
104.4	−0.005010	0.570
103.5	−0.007020	0.750
104.3	−0.006010	0.680
104.9	−0.005010	0.490
106.0	−0.003004	0.310

Table V. Experimental Data and Parameters for 2-Methyl-1-propanol–Tetrachloroethene at 760 ± 1 mmHg Pressure

t, °C	x_1	y_1
114.9	0.048	0.208
111.9	0.086	0.279
111.3	0.099	0.318
109.1	0.114	0.325
107.9	0.138	0.360
107.0	0.157	0.390
106.4	0.192	0.408
104.0	0.334	0.486
103.5	0.516	0.562
103.2	0.542	0.578
102.9	0.662	0.635
104.4	0.739	0.684
103.5	0.773	0.708
104.3	0.776	0.708
104.9	0.845	0.776
106.0	0.925	0.845

model	A_{12}[a]	A_{21}	α_{12}	mean deviation in y
Margules	1.3224	1.2320		0.0140
Van Laar	1.3245	1.2322		0.0140
Wilson	749.4093	443.0905		0.0135
NRTL	412.799	668.4601	0.2905	0.0134
	5.9088	329.3972		0.0134

[a] Equal to $\lambda_{ij} - \lambda_{jj}$ in Wilson, $g_{ij} - g_{jj}$ in NRTL, and $U_{ij} - U_{jj}$ in UNIQUAC. Units are cal/mol.

The exponential term is called the Poynting correction factor. At low and moderate pressures, this factor seldom deviates from unity. If the liquid-phase fugacity coefficient is neglected, eq 1 is reduced to

$$\gamma_i = \phi_i \pi y_i/(P_i^0 x_i) \qquad (2)$$

According to Hudson and Van Winkle (*5*), the vapor-phase fugacity coefficient can be ignored for most real systems at atmospheric pressure. Hence, eq 2 becomes

$$\gamma_i = \pi y_i/(P_i^0 x_i) \qquad (3)$$

The liquid-phase activity coefficients for the 2-methyl-1-propanol–tetrachloroethene system were calculated by using eq 2 and taking

$$\phi_i = \exp\{(B_i - V_i)(\pi - P_i^0)/(RT)\} \qquad (4)$$

The second virial coefficient for 2-methyl-1-propanol was estimated from the equation (*13*)

$$\log(-B_i) = 14.711 - 4.5 \log T \qquad (5)$$

Table VI. Experimental Data and Parameters for Tetrachloroethene–3-Methyl-1-butanol at 760 ± 1 mm Hg

t, °C	x_1	y_1
127.9	0.058	0.163
126.1	0.096	0.235
123.4	0.146	0.308
122.2	0.185	0.366
122.1	0.195	0.375
120.4	0.270	0.442
119.7	0.324	0.512
119.1	0.342	0.515
118.6	0.355	0.529
118.8	0.381	0.546
118.4	0.385	0.544
118.0	0.432	0.565
117.7	0.450	0.592
117.2	0.512	0.619
116.9	0.580	0.647
116.8	0.592	0.652
117.0	0.606	0.660
116.8	0.690	0.698
116.9	0.756	0.727
118.7	0.902	0.837
120.0	0.948	0.902

model	A_{12}	A_{21}	α_{12}	mean deviation in y
Margules	0.8844	1.1719		0.0057
Van Laar	0.0997	1.1926		0.0054
Wilson	293.9897	694.9781		0.0053
NRTL	830.5108	102.8085	0.2949	0.0053
UNIQUAC	301.2550	−40.9391		0.0054

Table VII. Pure-Component Properties (*2*)

component	V_i, mL/mol	r_i	q_i
2-methyl-1-propanol	92.91	3.4535	3.0480
3-methyl-1-butanol	109.22	4.1279	3.5880
tetrachloroethene	102.71	3.8879	3.4000

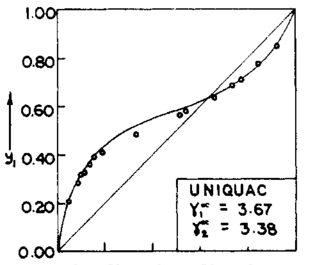

Figure 1. Equilibrium curve for 2-methyl-1-propanol–tetrachloroethene at 760 mmHg: (O) experimental; (—) UNIQUAC equation.

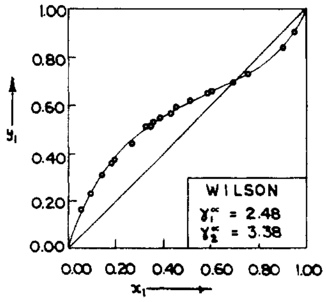

Figure 2. Equilibrium curve for tetrachloroethene–3-methyl-1-butanol at 760 mmHg: (O) experimental; (—) Wilson equation.

and that of tetrachloroethene from the Pitzer correlation (*9*). The molar volumes were calculated from the expression

$$V_i = a + bt + ct^2 \qquad (6)$$

The constants a, b, and c (Table III) were obtained by the procedure adopted by Prausnitz et al. (*10*) using the data on

Table VIII. Azeotropic Data of the Systems

solvent	alcohol	temp, °C			composition (mol % of solvent)		
		exptl	lit.[4]	computed (Meissner[7] method)	exptl	lit.[4]	computed (Meisner[7] method)
tetrachloroethene	2-methyl-1-propanol	102.8	103.05	107.89	39.0	40.13	37.32
tetrachloroethene	3-methyl-1-butanol	116.7	116.2	118.12	70.5	69.38	71.21

molar volumes available in the literature. The pure-component vapor pressures were obtained from the Antoine equations. The parameters of these equations are listed in Table III. The liquid-phase activity coefficients for this system were also calculated by using eq 3. From the activity-coefficient data thus calculated from eq 2 and 3, it is observed that the latter equation is a reasonable approximation for the 2-methyl-1-propanol–tetrachloroethene system. The effect of vapor-phase nonideality on the liquid-phase activity coefficents of 2-methyl-1-propanol is presented in Table IV. Further, the vapor-phase nonideality for the system tetrachloroethene-3-methyl-1-butanol can be neglected without losing accuracy because of the narrow range of equilibrium temperatures. Hence the liquid-phase activity coefficients of the components involved in the two binary systems were calculated by using eq 3. The experimental data are found to be thermodynamically consistent by the Herington test (*3*).

Several models, e.g., Margules (*6*), Van Laar (*14*), Wilson (*17*), NRTL (*12*), and UNIQUAC (*1*), are tested to represent the experimental liquid composition—activity coefficient data. The nonlinear simplex method modified by Nelder and Mead (*8*) with the following minimizing function was used for fitting activity coefficients to VLE data.

$$\sum_n \sum_i (\Delta\gamma_{i,n})_{\mathrm{rel}}{}^2 = \sum_n \sum_i [(\gamma_{\mathrm{exptl}} - \gamma_{\mathrm{calcd}})/\gamma_{\mathrm{exptl}}]_{i,n}{}^2 \qquad (7)$$

The parameters of the above-mentioned models for the two systems are presented in Tables V and VI along with the equilibrium data. The parameters were determined by using the pure-component properties given in Tables III and VII. Figures 1 and 2, show the x–y diagrams for the binary systems studied along with the limiting activity coefficients which were computed from the best correlating equation.

It is observed from the data that the binary mixtures of 2-methyl-1-propanol–tetrachloroethane and tetrachloroethene-3-methyl-1-butanol show positive deviations from Raoult's law, and the order of nonideality is as follows:

2-methyl-1-propanol > 3-methyl-1-butanol

These systems exhibit azeotropy. The experimental data are well compared with that of Horsley (*4*) and are presented in Table VIII along with the values computed by the method of Meissner and Greenfeld (*7*), which can predict the azeotropic temperature and composition up to an accuracy of ±2 °C and ±8 mol %, respectively. the experimental azeotropic data are confirmed by distilling the mixture in a laboratory-packed column.

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Glossary

A_{ij}	parameter in the Margules and Van Laar equations
B_i	second virial coefficient in eq 4, cm^3/mol
A, B, C	constants of the Antoine equation
a, b, c	Constants in the equation for molar volume
g_{ij}	interaction energy parameter in NRTL equation
n	number of components
P^0	pure-component vapor pressure, mmHg
q_i	pure-component area parameter of component i
r_i	pure-component volume parameter of component i
R	gas constant
t, T	equilibrium temperature, °C or K
U_{ij}	interaction energy parameter in UNIQUAC equation
V_i	molar volume of component i, cm^3/mol
$\bar{V}^L$	partial molar volume, cm^3/mol
x	mole fraction in liquid phase
y	mole fraction in vapor phase

Greek Letters

α_{ij}	nonrandomness parameter in NRTL equation
γ_i	activity coefficient of component i
λ_{ij}	interaction energy parameter in Wilson equation
π	total pressure, mmHg
ϕ	vapor-phase fugacity coefficient
$\phi_i{}^S$	liquid-phase fugacity coefficient

Subscripts

calcd	calculated
exptl	experimental
rel	relative
i, j	components i and j
1	more-volatile component
2	less-volatile component

Superscripts

∞	infinite dilution

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