Vapor–Liquid and Liquid–Liquid Equilibria in Binary Aqueous Systems

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Vapor–liquid equilibrium (VLE) data are reported in the miscible region for mixtures of 2-pentanol/water at 70, 80, and 90 °C and for 2-butanone/water at 60 and 70 °C. Mutual solubility data (LLE) were obtained from the literature. For these two binaries, VLE and LLE data were correlated with several models for the excess Gibbs energy. None of the currently popular models is able to represent both VLE and LLE using only two or three adjustable parameters. For simultaneous representation, a slightly modified Van Laar equation appears to be useful but, in general, this modification requires four binary parameters.

Introduction

Aqueous mixtures containing organic nonelectrolytes are often found in chemical technology; these mixtures are likely to become more interesting with advances in biotechnology. However, most organic nonelectrolytes are only partially miscible with water. It is therefore of interest to establish correlating methods which represent the thermodynamic properties of such mixtures with the requirement that both vapor–liquid equilibria (VLE) and liquid–liquid equilibria (LLE) are properly taken into account. This requirement is of particular importance for design of separations; an example is provided by the well-known process for obtaining pure ethanol from aqueous solution using benzene as an entrainer in extractive distillation.

Numerous authors have pointed out that common expressions for activity coefficients are not adequate for simultaneous representation of VLE and LLE in binary systems (e.g., ref *1* and *2*). If binary parameters in such an expression are adjusted to fit VLE data, the expression provides poor solubility limits and vice versa.

In this work, we report new experimental VLE data for two binary aqueous systems. We also report a comparison between observed and calculated VLE and LLE for these two binary aqueous systems. Calculations are based not only on the usual activity-coefficient models but also on some models that have only recently appeared in the literature.

Experimental Section

Vapor–liquid equilibria were measured by using a "Labodest" Phasengleichgewichte Apparatur (0601/U) manufactured by Fischer Gesellschaft (Fischer, Meckenheim, West Germany). This is a recirculating still of the type described by Walas (*3*).

The temperature was measured with a Fischer digital thermometer and the pressure with a Heise gauge. The Heise gauge was calibrated against a mercury manometer. Temperature measurements were accurate to 0.1 °C. The thermometer was calibrated against the vapor pressure of pure water as measured by the National Bureau of Standards. Pressure fluctuations during a typical run were usually less than 0.3% of the reported value which is accurate to 0.2 kPa.

All chemicals are commercially available. The purity of all chemicals, as measured by gas chromatography, was better than 99.8%.

Pure-component vapor pressures were also measured with the recirculating still. Measured and literature data agree to within 0.15%.

Liquid-phase compositions were measured with a gas chromatograph (GC). Samples of 1 μL in the organic-rich region and 0.2 μL in the water-rich region were withdrawn with a microliter syringe and analyzed with a Varian Model 3800 gas chromatograph using a thermal-conductivity detector. GC columns (4 m) were packed with Chromosorb 104(80/100 mesh) supplied by Waters Associates. GC response peaks were integrated by using a Varian Model CDS 111 chromatography data system. For the GC measurements, the important measured variables are the total carrier gas flow, peak area and retention time, column temperature, and column inlet and outlet pressures.

The retention data from the GC were calibrated with gravimetrically prepared standard solutions. GC calibration standards were stored in sealed septum bottles. Samples were analyzed until at least three consistent results were obtained.

The vapor sample separated into two phases when the temperature declined. To obtain accurate data, 1000-μL vapor samples were withdrawn and injected into sealed bottles, using acetone as a diluting agent to make the solution homogeneous. Then the sample was injected into the gas chromatograph. The accuracy of the vapor composition data was not critical, since it was used only as an estimate in the Barker (*4*) method to calculate vapor compositions from isothermal P–x data.

The still was heated until the contents started to boil. The pressure was then adjusted until boiling occurred at the desired temperature. Samples of liquid were analyzed repeatedly until consistent analyses were achieved.

The largest sources of experimental uncertainty were in the liquid-composition measurements. A single analysis of the liquid composition by gas chromatography is frequently imprecise. However, with multiple measurements, the standard deviation of the composition was less than 0.002.

Tables I and II give the experimental data (T, P, x). Three isotherms were measured for the 2-pentanol/water system. Two isotherms were measured for the 2-butanone/water system.

Data Reduction

A maximum-likelihood method (*5*) was used to regress the experimental VLE data. The regression gave parameters for 12 excess Gibbs energy functions identified in Table III. Vapor-phase corrections were included in the regressions; these were obtained from second virial coefficients (*10*, *11*).

Experimental LLE data were taken from the DECHEMA Chemistry Data Series (*12*, *13*) and verified with the original article. Mutual solubilities were calculated with the various activity-coefficient models using the two objective functions

$$a_1' - a_1'' = 0 \qquad (1)$$

$$a_2' - a_2'' = 0 \qquad (2)$$

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Table I. Total Pressures for the System 2-Pentanol (1)/Water (2)

70 °C		80 °C		90 °C	
P/mbar	$100x_1$	P/mbar	$100x_1$	P/mbar	$100x_1$
312.2	0	474.1	0	702.5	0
321.6	0.1	512.0	0.1	742.2	0.1
335.7	0.2	516.7	0.2	787.6	0.2
349.9	0.3	544.5	0.3	814.4	0.3
362.2	0.4	604.8	0.6	869.4	0.5
400.9	0.7	618.4	0.7	924.8	57.4
400.9	59.6	618.4	57.6	925.0	58.3
403.7	60.2	611.6	60.2	913.0	60.1
394.0	63.4	586.5	67.1	913.4	61.9
369.5	69.6	568.8	69.3	906.9	62.4
348.3	73.9	529.1	74.5	898.5	63.5
311.8	80.0	521.7	75.4	892.4	64.7
292.3	82.9	496.7	78.8	871.8	66.7
269.4	85.8	486.8	80.2	847.9	69.2
232.5	90.1	457.8	82.1	832.9	70.7
228.6	90.5	429.2	84.6	778.6	75.3
172.9	96.1	410.0	86.2	763.9	76.5
148.5	98.4	388.6	87.9	752.7	77.3
130.2	100	356.2	90.4	502.8	92.2
		270.0	96.2	465.5	94.0
		253.3	97.1	329.8	100
		211.1	100		

Solubility Data*100 (*12*)

70 °C		80 °C		90 °C	
x_1'	x_1''	x_1'	x_1''	x_1'	x_1''
0.69	59.6	0.70	57.6	0.72	55.2

Vapor-Pressure Data

water	311.66 (70)	473.63 (80)	701.08 (90)	(ref *10*)
2-pentanol	128.55 (70)	209.16 (80)	327.77 (90)	(ref *15*)
	129.84 (70)	210.48 (80)	328.70 (90)	(ref *16*)

Table II. Total Pressures for the System 2-Butanone (1)/Water (2)

60 °C		70 °C	
P/mbar	$100x_1$	P/mbar	$100x_1$
523.8	100	740.9	100
574.9	92.5	845.5	90.1
578.1	92.3	854.8	87.9
583.0	90.7	874.1	84.2
585.8	90.5	873.7	83.3
588.0	89.7	886.9	78.2
592.4	89.1	886.2	77.8
599.2	86.6	890.1	75.5
601.6	85.6	889.9	75.2
605.8	82.9	890.0	73.9
609.1	80.7	891.4	71.9
611.4	78.6	890.8	71.6
612.7	76.5	891.0	71.2
613.9	74.9	891.9	71.1
614.6	72.8	892.9	70.1
613.5	65.1	893.3	67.6
613.5	5.20	892.8	67.2
524.6	3.14	788.6	3.31
457.2	2.19	777.5	3.18
430.6	1.76	726.3	2.63
371.8	1.34	603.1	1.60
200	0	594.3	1.54
		582.3	1.48
		312.2	0

Solubility Data*100 (*13*)

60 °C		70 °C	
x_1'	x_1''	x_1'	x_1''
5.2	65.1	4.8	63.2

Vapor-Pressure Data

water	199.18 (60)	311.66 (70)	(ref *10*)
2-butanone	523.6 (60)	740.57 (70)	(ref *10*)

Table III. Activity-Coefficient Models Used for Comparing Observed and Calculated VLE and LLE

model	name	ref	no. of binary parameters
I	Redlich–Kister	*4*	4
II	Van Laar	*4*	2
III	NRTL	*4*	3
IV	UNIQUAC	*4*	2
V	Feix et al	*6*	2
VI	Tsuboka–Katayama	*7*	2
VII	Kreglewski–Hall	*8*	3
VIII	Wang–Chao ($\alpha = 1$, $Z = 6$)	*9*	2
IX	Wang–Chao ($\alpha = 0.6$, $Z = 6$)	this work	3
X	Wang–Chao ($\alpha = 1$, $Z = 10$)	this work	2
XI	Wang–Chao ($\alpha = 0.6$, $Z = 10$)	this work	3
XII	modified Van Laar	this work	4

Table IV. Infinite-Dilution Activity Coefficients and Miscibility Limits for the System 2-Pentanol (1)/Water (2) at 90 °C from Models for the Excess Gibbs Energy

model	γ_1^∞	γ_2^∞	$100x_1'$	$100x_1''$
I	123.0	3.45	0.67	59.0
II	122.0	3.59	0.70	60.9
III	127.0	3.99	0.69	59.0
IV	121.0	3.58	0.71	61.0
V	129.0	3.89	0.72	58.9
VI	126.0	3.75	0.71	59.9
VII	118.0	4.01	0.70	60.6
VIII	143.0	5.44	0.72	47.6
IX	142.6	4.02	0.82	57.9
X	131.1	3.95	0.73	58.9
XI	131.2	3.94	0.81	62.2
XII	122.6	3.60	0.72	55.2
exptl	126 ± 6	3.8 ± 0.2	0.72	55.2

Table V. Infinite-Dilution Activity Coefficients and Miscibility Limits for the System 2-Butanone (1)/Water (2) at 70 °C from Models for the Excess Gibbs Energy

models	γ_1^∞	γ_2^∞	$100x_1'$	$100x_1''$
I	31.7	7.26	4.88	58.3
II	30.0	6.04	4.53	71.9
III	32.4	7.18	5.12	63.9
IV	31.6	6.52	4.90	69.1
V	32.1	6.5	4.99	68.9
VI	33.3	7.01	5.39	64.8
VII	31.5	7.46	4.82	59.1
VIII	37.3	7.72	7.01	52.9
IX	37.0	7.04	6.48	64.2
X	33.7	6.54	5.25	68.9
XI	33.7	6.54	5.25	68.9
XII	30.02	6.04	4.80	63.2
exptl	29.5 ± 2.5	6.4 ± 0.2	4.8	63.2

where $'$ and $''$ refer to the two liquid phases and a refers to activity.

Results

Tables IV and V compare calculated and experimental infinite-dilution activity coefficients for the two systems at the highest isotherms measured. The miscibility limits are also compared.

Of the currently popular Gibbs energy models (I–VIII in Table III), the Redlich–Kister (I) and Wang–Chao (VIII) models give the best results for representing both VLE and LLE for most of the binary systems. Models III and V give fair results.

To improve representation of both VLE and LLE behavior by the Wang–Chao equation, two modifications were examined.

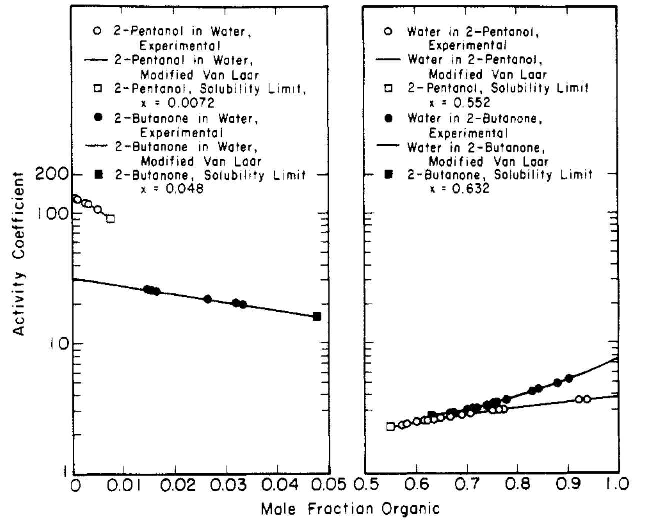

Figure 1. Activity coefficients in aqueous solutions: 2-pentanol at 90 °C and 2-butanone at 70 °C.

In the Wang–Chao model, the molar excess Gibbs energy is given by

$$g^{\mathrm{E}} = \frac{Z}{2}[x_1x_{21}(g_{21} - g_{11}) + x_2x_{12}(g_{12} - g_{22})] + RT\left(x_1 \ln \frac{\phi_{11}}{x_1} + x_2 \ln \frac{\phi_{22}}{x_2}\right) \quad (3)$$

where Z is the coordination number and the local mole fractions are given by

$$x_{21} = \frac{x_2 \exp(-\alpha g_{21}/RT)}{x_1 \exp(-\alpha g_{11}/RT) + x_2 \exp(-\alpha g_{21}/RT)} \quad (4)$$

and x_{12} is given by eq 4 with subscripts 1 and 2 everywhere exchanged.

In their original work (*9*), Wang and Chao set $\alpha = 1$ and $Z = 6$. In the first modification, the coordination number Z is set equal to 10. This change showed only small improvement. In the second modification, parameter α (similar to that in the NRTL equation) was adjusted. When α is about 0.6, some improvement is obtained, but consistent quantitative agreement with both VLE and LLE data cannot be attained. Similar partial improvement is obtained when calculations are performed for 12 representative binary aqueous systems (containing ketones, ethers, or alcohols). These calculations, not presented here, support our conclusion that none of the common models for the excess Gibbs energy is reliable for reproducing VLE and LLE using the same parameters.

To obtain better results, we suggest a modification of the classical Van Laar model; this modification is similar to the one proposed by Black (*14*). We suggest that the molar excess Gibbs energy be written

$$\frac{g^{\mathrm{E}}}{RT} = \frac{x_1x_2A_{12}A_{21}}{A_{12}x_1 + x_2A_{21}}[1 + C(x_1 - x_2) + D(x_1 - x_2)^2] \quad (5)$$

The leading term is the Van Laar equation; empirical coefficients C and D are small compared to unity.

To obtain the binary coefficients, we first reduce VLE data with the initial assumption that $C = D = 0$. This procedure gives good initial values for coefficients A_{12} and A_{21}. We then refit the VLE data with the additional objective functions given by the LLE data (eq 1 and 2) to obtain the binary coefficients. For the 2-pentanol and 2-butanone systems we also compare observed and calculated activity coefficients at infinite dilution and observed and calculated mutual solubilities (model XII in Tables IV and V). For all of the representative binary aqueous systems, we find that while small values of C and D can have a large effect on calculated LLE, they have only a small effect on calculated VLE.

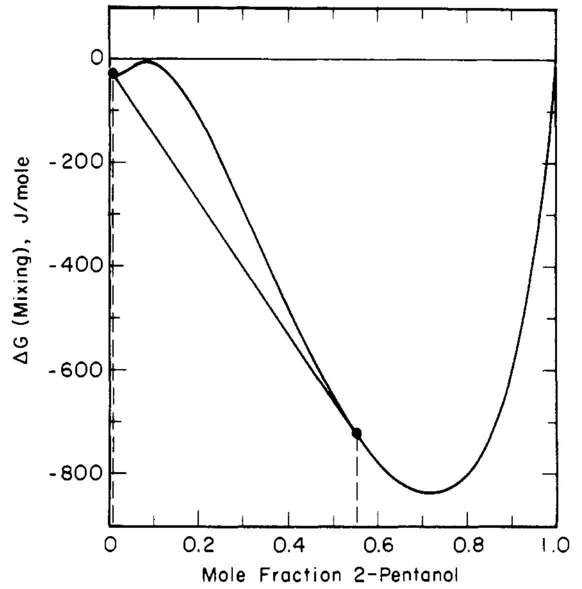

Figure 2. ΔG(mixing) for the 2-pentanol/water system at 90 °C.

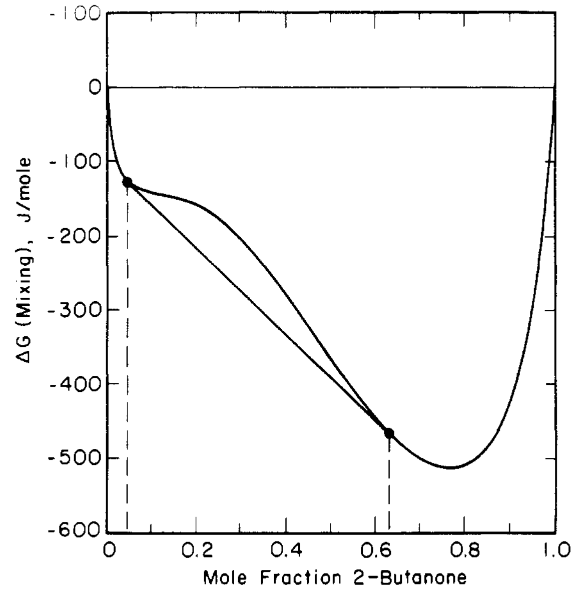

Figure 3. ΔG(mixing) for the 2-butanone/water system at 70 °C.

Figure 1 shows the modified Van Laar representation of the activity coefficients for the 2-pentanol and 2-butanone systems. The calculated and experimental values agree quite well.

Figures 2 and 3 show the calculated ΔG(mixing) for the modified Van Laar model for the two systems. The mutual solubilities determined from this model agree exactly with the published experimental values.

The modified Van Laar model appears to be useful for simultaneous representation of VLE and LLE in binary aqueous systems. However, such representation is only successful if the necessary parameters are evaluated from both VLE and LLE data. As yet, we have no adequate model for reliable prediction of LLE from VLE data alone, or vice versa. Nevertheless, reliable simultaneous representation of experimental VLE and LLE data may be useful for simulation in computer-aided process design.

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Registry No. 2-Pentanol, 6032-29-7; 2-butanone, 78-93-3.

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Mutual Solubilities in Six Binary Mixtures of Water + a Heavy Hydrocarbon or a Derivative

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Mutual solubilities at the three-phase vapor–liquid–liquid equilibrium pressure were experimentally determined for six binary mixtures of water with *m*-cresol, quinoline, indoline, 1,2,3,4-tetrahydroquinoline (THQ), thianaphthene, or 9,10-dihydrophenanthrene at temperatures from 293 to 502 K. The equilibrium compositions of both liquid phases, temperature, and three-phase equilibrium pressure are reported.

Introduction

The fluid phase equilibrium of hydrocarbon and water mixtures is of fundamental interest in the chemical, petroleum, and natural gas industries. Much is known about the solubilities of hydrocarbons and water at temperatures close to ambient. High-temperature data are available only for a limited number of paraffinic, olefinic, and naphthenic hydrocarbons and for a few aromatic hydrocarbons.

Schneider and co-workers (*1–6*) reported solubility data for binary mixtures of water with several alkanes, alkylated benzenes, phenol, biphenyl, tetralin, and *cis*- and *trans*-decalin at temperatures up to 693 K and pressures to 370 MPa. Skripka and co-workers (*7–11*) studied the phase behavior of water in mixtures with heavy *n*-alkanes (up to *n*-eicosane) at temperatures from 323 K to the three-phase critical point and at pressures to 79 MPa. Wilson and co-workers (*12*, *13*) recently investigated the mutual solubilities of hydrocarbons and water along the three-phase locus to temperatures and pressures approaching the critical end point. Compositions, temperature, and pressure were reported for aqueous hydrocarbon systems of several paraffins, olefins, naphthenes, light aromatics, 1-methylnaphthalene, and 1-ethylnaphthalene.

We report in this work the mutual solubilities of water and six polycyclic aromatic hydrocarbons, which are of interest to the processing of coal and heavy oils. The hydrocarbons studied include N-, O-, and S-containing heteronuclear aromatics and a three-ring aromatic.

Experimental Apparatus

The measurements of this work were made in a recirculating static apparatus. Figure 1 shows the schematic diagram. The heart of the apparatus is the equilibrium cell, which is made from a clear flat insert gauge (Eugene Ernst Products Model EEPWT-15) rated to 10 MPa at 593 K. The cell body is 316 stainless steel and has an internal volume of approximately 100 cm^3. Tempered glass windows enclose the cell on opposing sides for visual observation of the phases. All feed and sample tubing connections to the cell, including a dip tube for sampling of the upper liquid layer, are mounted into the cell end plugs. Samples are withdrawn from the equilibrated phases through $^1/_{16}$-in. 316 stainless steel tubing. The cell temperature is measured by a calibrated type K thermocouple inserted into the cell body. The thermocouple was calibrated to an accuracy of ±0.1 K. A Model CMM 0–500 psi Heise gauge measures pressure in the cell to 0.1% of the maximum range. The cell is submerged in a thermostated silicone oil bath (Dow Corning 550 silicone fluid) controllable to within ±0.1 K over the range of 333–513 K.

To promote the attainment of equilibrium, the cell contents are mixed by means of a magnetic recirculation pump submerged in the oil bath. The pump is similar to that described by Ruska and co-workers (*14*). The function of the pump is to withdraw the fluid of the heavier phase from the bottom of the equilibrium cell and discharge the fluid into the headspace of the cell. By judicious adjustment of pump drive speed, adequate mixing is achieved without the creation of stable emulsions. Recirculation rates on the order of 10–30 cm^3/min have been found satisfactory.

The hydrocarbon of interest and water were fed to the equilibrium cell by positive displacement pumps. Enough feed material was added to diminish the cell vapor volume to a mere indicator bubble and to position the liquid–liquid interface at about the center of the cell. The cell contents were then recirculated by magnetic pump and heated to the desired temperature. The liquids were degassed by repeatedly bleeding vapor from the top of the cell until the cell pressure no longer changed with bleeding.

Before withdrawal of the samples from the liquid phases at equilibrium, the liquids in the cell were recirculated for 5–30 min and then allowed to stand and settle. The temperature and pressure were recorded. Liquid samples of each phase were withdrawn from the cell via insulated $^1/_{16}$-in. tubing under cell pressure. In case the three-phase equilibrium pressure was lower than atmospheric pressure, the cell was pressurized with

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