many fundamental studies of systems involving water as a reactant, qualified by the possible uncertainties of extrapolation into regions where experimental and/or correlating data do not exist.

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Vapor–Liquid Equilibrium of the Mixtures 2-Furaldehyde/1-Butanol and 2-Furaldehyde/4-Methyl-2-pentanone

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Low-pressure isothermal vapor–liquid equilibrium has been measured for pure 2-furaldehyde and for 2-furaldehyde separately with 1-butanol and 4-methyl-2-pentanone. Because of the ease with which 2-furaldehyde both oxidizes and autoxidizes, special handling methods had to be developed. Activity coefficients derived from our data have been correlated with five thermodynamic models and used to estimate UNIFAC group contribution parameters.

Introduction

Furfural or 2-furaldehyde is used in many industrial processes, including as a selective solvent for separating saturated from unsaturated hydrocarbons, in the extractive distillation of C_4 and C_5 hydrocarbons, and as a chemical from which a variety of aliphatic and heterocyclic compounds can be synthesized. In the UNIFAC (*1*, *2*) group contribution method of predicting activity coefficients, furfural is treated as a single group. In spite of its industrial importance, relatively few data on the binary vapor–liquid of mixtures containing furfural appear in the literature (*3*). Thus, UNIFAC parameters are not available for the interactions of many groups with furfural. For this reason we chose to measure the vapor–liquid equilibrium of furfural with an alcohol and a ketone, each along two isotherms. There are no previously reported data for the systems we have measured.

Experimental Section

The general equipment and procedures we used have been discussed previously (*4*). Therefore, the discussion here will be mainly concerned with the special problems and procedures involved in using furfural. Furfural is an extremely hazardous chemical (2 ppm allowable exposure concentration over an 8-h day); in addition, it is easily absorbed through the skin and dangerous to the eyes. Furfural is not very stable; it is especially susceptible to oxidation, though it also decomposes by reactions with acid and by heat (*5*–*7*). A very sensitive indication of oxidation is a change in color. Immediately after purification (using a 13-stage Oldershaw column at low pressure under a nitrogen blanket) a clear liquid was obtained. Upon exposure to even small amounts of oxygen, the color changed to yellow, and then yellow/brown in several hours at room temperature, and more rapidly at elevated temperatures. Using a gas chromatograph/mass spectrograph unit, we have found that the main oxidation product is 2-fuoric acid. We tried several oxidation reaction inhibitors as suggested by Dunlop et al. (*5*) including triethylamine, tripropylamine, and hydroquinone but all were ineffective at the temperatures of our experiments.

Several major changes in our equipment and operating procedure had to be made in order to make the measurements we report here. First, all traces of water and oxygen had to be kept out of the system. This included even trace amounts used in the nitrogen blanket in the purification and measurement steps. Thus we started with Grade 5 nitrogen, which was then passed through a steel column containing one layer of manganese(II) oxide and another of molecular sieves, before entering our system. Second, tubing to permit the direct transfer

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Table I. Measured Vapor Pressures and Coefficients of the Antoine Equation

a. Measured Vapor Pressures

furfural		4-methyl-2-pentanone		1-butanol	
T_{expt}, K	P_{expt}, kPa	T_{expt}, K	P_{expt}, kPa	T_{expt}, K	P_{expt}, kPa
365.760	9.950	356.540	35.612	350.565	19.295
370.116	11.938	359.287	39.195	353.492	22.205
371.820	12.685	363.183	44.853	356.013	24.911
375.870	14.830	365.467	48.580	358.326	27.717
379.443	17.175	367.962	52.675	361.186	31.423
382.725	19.425	370.577	57.465	362.281	33.000
384.570	21.000	373.531	63.192	364.891	36.938
387.545	23.250	376.171	68.665	367.702	41.640
389.800	25.060	380.250	78.002	370.596	46.987
391.845	26.955	383.071	84.970	373.240	52.288
393.780	28.929	385.185	90.493	375.804	57.910
		387.992	98.355	378.265	63.832
				380.795	70.347
				382.310	74.428
				382.353	74.571
				385.915	85.133
				387.598	90.480

b. Antoine Equation[a]

	A	B	C
furfural	12.85146	2622.270	−117.4089
1-butanol	14.69018	2861.851	−106.5737
4-methyl-2-pentanone	14.35323	3258.354	−54.30857

[a] $\ln P\ (\text{kPa}) = A - B/[T(\text{K}) + C]$.

Table II. Measured Vapor Pressures of Furfural Compared to Values Calculated from Correlation of Matthews (*9*) and Vapor Pressure Measured by Others[a]

a. Vapor Pressures Measured in This Work

T, K	P_{expt}, kPa	P_{calcd}, kPa	dev, kPa
365.760	9.950	10.208	−0.258
370.116	11.938	12.228	−0.290
371.820	12.685	13.102	−0.416
375.870	14.830	15.382	−0.552
379.443	17.175	17.653	−0.477
382.725	19.425	19.970	−0.544
384.570	21.000	21.376	−0.375
387.545	23.250	23.810	−0.560
389.800	25.060	25.809	−0.748
391.845	26.955	27.716	−0.761
393.780	28.929	29.634	−0.704

b. Vapor Pressure of Furfural Measured by Others[a]

T, K	measd P, kPa	Antoine P, kPa	source of exptl data
391.65	26.663	26.831	*11*
403.75	39.995	40.190	*11*
366.48	11.706	10.209	*12*

[a] Compared to calculations from our Antoine equation.

Table III. Measured Vapor–Liquid Equilibrium of 1-Butanol (1)/Furfural (2) at 368.15 K

P, kPa	x_1	y_1	P, kPa	x_1	y_1	P, kPa	x_1	y_1
10.973	0.000	0.000	32.708	0.419	0.781	38.593	0.713	0.869
16.785	0.068	0.405	32.895	0.422	0.782	39.550	0.784	0.891
20.483	0.120	0.525	33.908	0.466	0.796	39.882	0.800	0.900
25.452	0.211	0.655	34.270	0.489	0.811	40.755	0.859	0.922
29.620	0.314	0.735	36.243	0.578	0.832	41.572	0.928	0.952
31.147	0.361	0.757	37.133	0.631	0.844	42.410	1.000	1.000

Table IV. Measured Vapor–Liquid Equilibrium of 1-Butanol (1)/Furfural (2) at 383.15 K

P, kPa	x_1	y_1	P, kPa	x_1	y_1	P, kPa	x_1	y_1
19.761	0.000	0.000	57.852	0.435	0.791	69.840	0.750	0.889
33.953	0.109	0.476	59.948	0.482	0.806	72.176	0.826	0.917
47.140	0.250	0.683	61.349	0.506	0.812	74.565	0.910	0.949
51.228	0.312	0.725	64.542	0.590	0.838	76.919	1.000	1.000
54.202	0.361	0.754	67.463	0.675	0.867			

Table V. Measured Vapor–Liquid Equilibrium of 4-Methyl-2-pentanone (1)/Furfural (2) at 368.09 K

P, kPa	x_1	y_1	P, kPa	x_1	y_1	P, kPa	x_1	y_1
10.973	0.000	0.000	24.671	0.240	0.639	41.439	0.675	0.898
12.402	0.020	0.128	26.891	0.290	0.689	43.930	0.745	0.923
14.230	0.046	0.259	29.760	0.348	0.739	46.550	0.822	0.948
16.440	0.078	0.371	32.104	0.413	0.782	49.148	0.892	0.968
18.610	0.117	0.477	33.855	0.461	0.814	52.994	1.000	1.000
20.180	0.144	0.526	35.810	0.513	0.838			
22.943	0.196	0.603	38.190	0.581	0.862			

of furfural between the purification still and the Stage–Muller still used in our measurements was installed. Also, the sampling areas and equilibrium chamber were isolated so that any oxygen which may have entered during the sampling procedure was kept out of the boiling flask and equilibrium chamber. All additions and removals of chemicals were done with a transfer needle and septa. Finally, an initial charge of furfural was boiled in the still and then discarded. Therefore, during the oxidation, the furfural itself removed any traces of oxygen which may have entered the system. Even with all these precautions, only two or three data points could be taken before a slight color change was evident in furfural-rich systems. When such a change was noticed, the still contents were removed and replaced. In the furfural vapor pressure measurements, each point taken after refilling the still overlapped the previous point. In this way we established that excellent reproducibility was obtained as long as the change in color (to a pale yellow) was slight.

Separate from the oxidation problems, furfural was difficult to work with because of its tendency to superheat and its high surface tension, both of which result in periodic flooding of the Stage–Muller still. Because of these problems, and in spite of all precautions we took, we were able to maintain temperature constant to only ±0.03 K in solutions containing more than 50 mol % furfural, while the temperature could be maintained constant to within ±0.012 K or less in solutions dilute in furfural.

All the chemicals used in our work were Gold Label quality obtained from Aldrich Chemicals, and all were purified by distillation. The furfural was handled as described above, and the 1-butanol was dried with molecular sieves since initial measurements indicated contamination by water.

Before the mixtures were studied, the vapor pressures of each of the three pure components were measured in the Stage–Muller still. The results appear in Table I, together with the Antoine coefficients fitted to our data. While our data for 1-butanol and 4-methyl-2-pentanone agree with previous work (*8*, *9*), Table II shows that our vapor pressure data for furfural are systematically below those of Matthews (*10*), the most complete data set available covering our temperature range. Further, also shown in Table II, are the less complete data of Rivenq (*11*) and of Welty et al. (*12*). Since none of the other investigators mentioned the possibility of furfural oxidation, and apparently took no special precautions to avoid it, and since the oxidation products raise the apparent vapor pressure of furfural, we believe our data to be correct. Further, a Clausius–Clapeyron plot (ln P^{vap} vs. $1/T$) of our furfural data gives an excellent straight line.

In our study of mixtures, all compositional analyses were done with a gravimetrically calibrated Hewlett-Packard 5730A gas chromatograph with a 3390A integrator. A thermal conductivity detector, maintained at 250 °C, was used, with a 6 ft × $^1/_8$ in. Porapak column. A Type P80/100 column at 170 °C was used for the furfural/4-methyl-2-pentanone measurements, and a Type QS column at 180 °C was used with furfural and 1-butanol. Other than the fact that the still was frequently

Table VI. Measured Vapor-Liquid Equilibrium of 4-Methyl-2-pentanone (1)/Furfural (2) at 383.09 K

P, kPa	x_1	y_1	P, kPa	x_1	y_1	P, kPa	x_1	y_1
19.761	0.000	0.000	42.515	0.260	0.644	66.658	0.672	0.888
25.003	0.047	0.241	47.198	0.325	0.704	72.568	0.775	0.926
28.945	0.085	0.365	50.958	0.385	0.746	78.138	0.872	0.957
33.685	0.143	0.493	56.460	0.484	0.813	85.002	1.000	1.000
36.829	0.185	0.561	61.355	0.575	0.853			

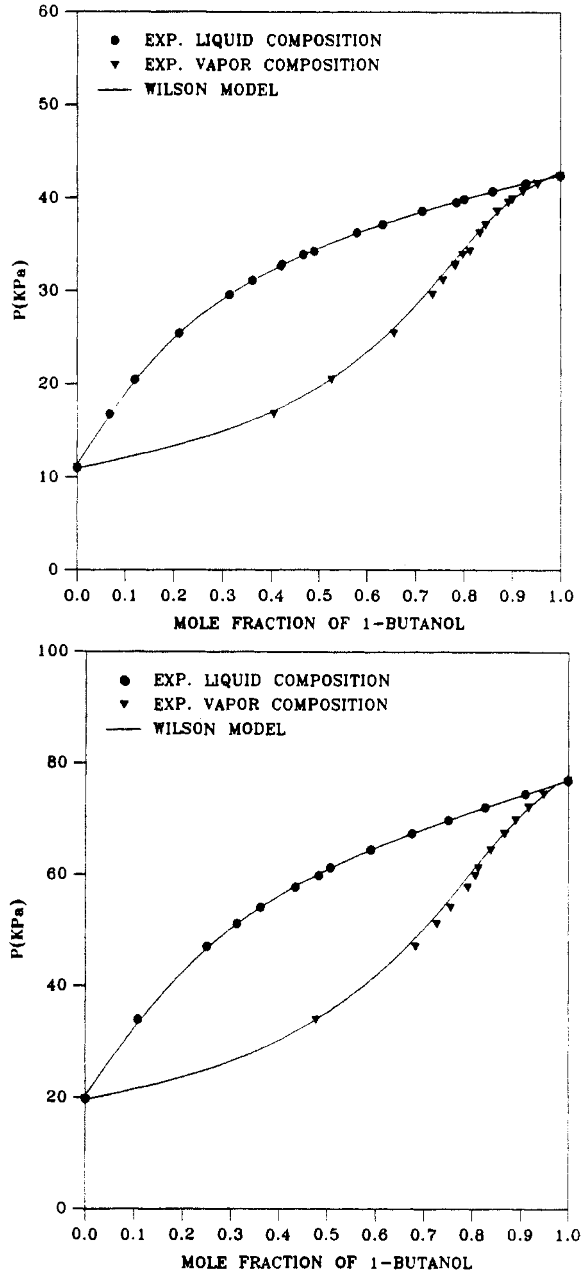

Figure 1. Measured vapor-liquid equilibrium of 1-butanol and furfural at (a, top) 368.15 and (b, bottom) 383.15 K.

emptied and refilled (because of the autoxidation of furfural), the measurement procedures are as we have described them previously. The results of our measurements appear in Tables III-VI, and are plotted in Figures 1 and 2. As can be seen, neither of the systems studied has an azeotrope.

Consistency Test and Discussion of Results

We have used two consistency tests on our data. The first is the point-to-point consistency test of Fredenslund et al. (*1*) using a third order Legendre polynomial and assuming the vapor phase to be an ideal gas, or describable by a two-term virial series with virial coefficients predicted by the correlations of Hayden and O'Connell (*13*) and of Tsonopolous (*14*). For all cases, the average absolute deviation in pressure was less than 0.2 kPa for the furfural/4-methyl-2-pentanone system and less than 0.1 kPa for the 1-butanol/furfural system. The average absolute deviation in the vapor-phase mole fractions was 0.007 and 0.0085, respectively, for these two systems. The virial coefficients and liquid molar volumes used in these calculations appear in Table VII. The use of the Tsonopolous correlation led to the greatest absolute deviations in the vapor-phase mole fraction; therefore this correlation is not considered further. While the absolute average deviations in the pressure in our measurements are similar to those we have obtained previously, the deviations in vapor-phase mole fraction are slightly greater. This is not unexpected, because of the difficulty in working with furfural.

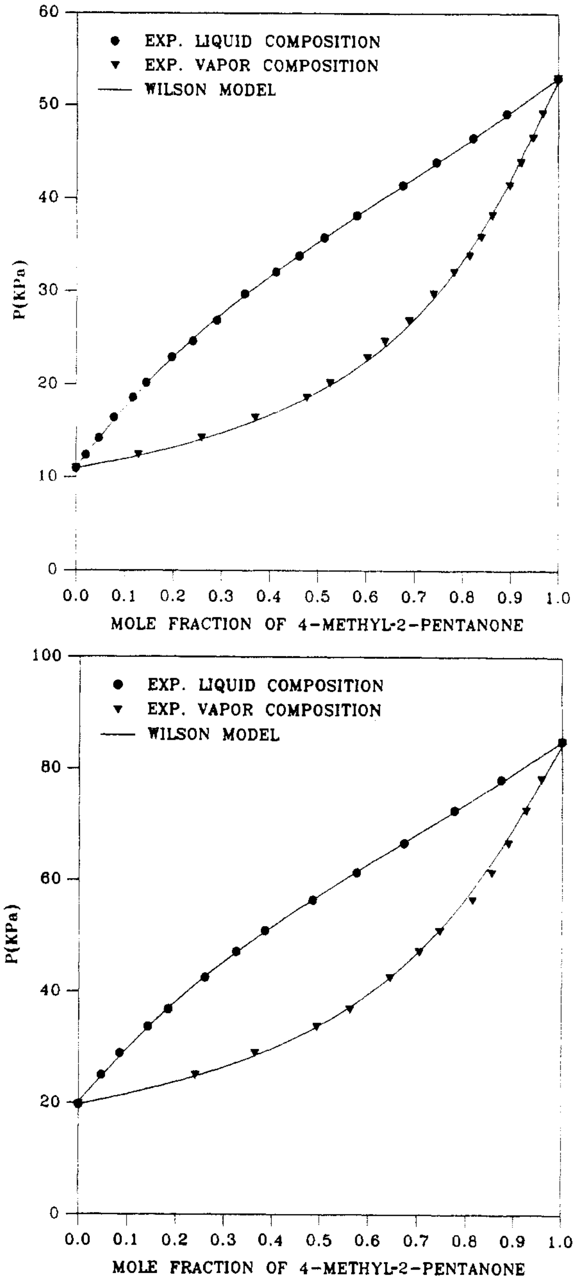

Figure 2. Measured vapor-liquid equilibrium of 4-methyl-2-pentanone and furfural at (a, top) 368.09 and (b, bottom) 383.09 K.

Fredenslund et al. (*1*) suggest that the absolute value of $y_{\mathrm{expt}} - y_{\mathrm{calcd}}$ should be less than 0.01 for thermodynamically consistent data. While much of our data satisfies this consistency test, some do not, again not unexpected because of the diffi-

Table VII. Virial Coefficients and Liquid Molar Volumes Used in Calculations

system	T, K	Hayden–O'Connell virial coeff, cm^3/mol B_1	B_2	B_{12}	liq molar vol, cm^3/mol V_1	V_2
4-methyl-2-pentanone/furfural	368.09	−3153	−1996	−1114	143.2	117.6
	383.09	−2200	−1730	−987	146.2	119.0
1-butanol/furfural	368.15	−1532	−1994	−859	103.3	117.6
	383.15	−1213	−1729	−769	105.6	119.0

Wilson Model[a]

		AADP, kPa	AADY	A_{12}	A_{21}
		4-Methyl-2-pentanone/Furfural			
ideal gas phase	T = 368.09 K	0.08	0.0049	0.611 59	1.004 19
	T = 383.09 K	0.20	0.0041	0.569 02	1.083 84
real gas phase, ref 13	T = 368.09 K	0.09	0.0051	0.672 79	0.871 64
	T = 383.09 K	0.21	0.0049	0.633 24	0.938 29
		1-Butanol/Furfural			
ideal gas phase	T = 368.15 K	0.05	0.0067	0.671 32	0.454 65
	T = 383.15 K	0.08	0.0077	0.745 63	0.477 73
real gas phase, ref 13	T = 368.15 K	0.05	0.0077	0.663 61	0.451 28
	T = 383.15 K	0.08	0.0092	0.732 85	0.473 85

[a] $A_{12} = \lambda_{12} - \lambda_{11}$; $A_{21} = \lambda_{21} - \lambda_{22}$.

Table VIII. UNIFAC Interaction Parameters and Predictions Using the Parameters

a. UNIFAC Interaction Parameters

system	T, K	CH_2CO–furfural	furfural–CH_2CO
4-methyl-2-pentanone/furfural	368.09	−16.107	53.527
	383.09	−45.870	83.006
both temp simult		−15.619	51.983
ref *2*		−163.7	317.5
1-butanol/furfural		OH–furfural	furfural–OH
	368.15	2410.265	−105.304
	383.15	1583.883	−122.707
both temp simult		350.191	33.735
ref *2*		−120.5	521.6

b. Predictions Using UNIFAC Parameters

system	T, K	lit. parameters AADY	AADP, kPa	new parameters AADY	AADP, kPa
4-methyl-2-pentanone/furfural	368.09	0.0265	1.51	0.0108	0.48
	383.09	0.0246	2.73	0.0091	0.96
1-butanol/furfural	368.15	0.0226	0.72	0.0098	0.29
	383.15	0.0248	1.52	0.0130	0.43

culty in working with furfural. Interestingly, all of our data sets satisfy the Gibbs–Duhem equal-area consistency test.

We have fit our data with five different, two-constant activity coefficient models: the three-suffix Margules, van Laar, Wilson, NRTL, and UNIQUAC models. The goodness of fit was marginally best with the Wilson equation, and decidedly poorest with the UNIQUAC model; slightly better results were obtained assuming the vapor phase to be an ideal gas. We have shown, in Figures 1 and 2, the Wilson model fit to our experimental data. The absolute average deviations in P and y, and the Wilson model parameters are also given in Table VII. Note that while the choice of ideal gas or the virial equation for the vapor phase has little effect on the absolute average deviations, it does result in larger variations in the liquid–phase activity coefficient model parameters. In all cases, to obtain these parameters, the maximum likelihood method was used with the objective function discussed in a previous paper (*15*).

Since there are so little data available on mixtures containing furfural, we have computed the furfural–ketone and furfural–OH parameters from our data using values reported in the literature (*2*) for all other group contribution interaction parameters. The value of the parameters we have obtained along each isotherm, and by fitting both isotherms simultaneously, are shown in Table VIII together with the previously UNIFAC parameters. Data in the table also show that the use of the new parameters results in a decrease, by a factor of 2 to 3, in the absolute average deviations in P and y for our data. However, it would be more advantageous for our data to be used in one of the periodic reevaluations of all UNIFAC parameters rather than, as we have done here, evaluate some parameters while keeping others fixed.

Conclusions

In this communication, we have reported low-pressure vapor–liquid equilibrium measurements for furfural with, separately, an alcohol and a ketone. In this work we have found furfural to be easily oxidizable, so that special methods of purifying and handling it had to be developed. We believe our vapor pressure data for furfural to be the most accurate presently available. Further, since data for the mixtures we have studied, furfural/1-butanol and furfural/4-methyl-2 pentanone, both at 368 and 383 K, were not previously available, our data should be of interest in engineering design and in the estimation of group contribution parameters.

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