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Mixture Properties of the Water + γ-Butyrolactone + Tetrahydrofuran System. 3. Isobaric Vapor–Liquid Equilibrium of Water + γ-Butyrolactone and Tetrahydrofuran + γ-Butyrolactone at 1.013 bar

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Isobaric vapor–liquid equilibrium data have been determined indirectly at 1.013 bar by measuring *T*–*x* data of the systems (I) tetrahydrofuran (THF) + γ-butyrolactone (GBL) and (II) water + GBL using a Swietoslawski type ebulliometer. Experimental data have been regressed to minimize the deviations in the boiling temperatures for all the points, and Wilson equation parameters and vapor-phase compositions are reported.

Introduction

In continuation of the work on the property measurements of tetrahydrofuran (THF) + γ-butyrolactone (GBL) + water system, we have earlier presented enthalpies of mixing (*1*), equilibrium properties, and transport properties of THF + GBL and water + GBL systems (*2*, *3*). In the present investigation we are reporting the vapor–liquid equilibrium data for THF + GBL and water + GBL at 1.013 bar pressure. Critically evaluated VLE data are available for THF + water system at 1.013 bar in the literature (*4*). Some subatmospheric data (0.2667–0.80 bar) have been reported for water + GBL (*5*). Hence, with the present data and in conjunction with the literature data on THF + water, VLE of the ternary system THF + water + GBL can be evaluated at 1.013 bar. This ternary system is the major product in the oxidation of THF to GBL.

Experimental Section

The method of purification and purity of samples is given in part 1 (*2*). A Swietoslawski type ebulliometer was used to measure the *T*–*x* data at 1.013 bar. The details of equipment and operational procedure have been reported elsewhere (*6*). Pressure was read up to 1 mmHg with a U-tube mercury manometer having an inside diameter of 0.014 m. Temperatures were measured accurately to ±0.025 K by use of a platinum resistance thermometer (R_0 = 100 Ω) supplied by Minco Products, U.S.A.

Table I. *T*–*X* Data for THF + GBL at 1.013 bar

x_{THF}	T/°C	y_{THF}	$T_{expt} - T_{calc}$[a]
0.0276	178.12	0.5421	1.70
0.1076	132.15	0.9039	-1.76
0.2108	111.18	0.9689	2.15
0.2997	96.10	0.9835	-1.06
0.4142	86.55	0.9909	-0.89
0.4991	82.48	0.9937	0.01
0.6044	78.00	0.9958	0.15
0.7009	75.12	0.9970	0.53
0.8046	71.20	0.9980	-0.50
0.9047	69.22	0.9990	0.08
0.9574	67.08	0.9995	-0.66
mean dev			0.86
max dev			2.15

[a] T_{calc} is the bubble-point temperature calculated by using the Wilson model.

Table II. *T*–*x* Data for Water + GBL at 1.013 bar

x_{water}	T/°C	y_{water}	$T_{expt} - T_{calc}$[a]
0.0612	163.98	0.7133	0.92
0.1077	147.90	0.8473	1.55
0.2036	125.28	0.9319	-2.31
0.2913	117.70	0.9571	-0.65
0.4068	110.50	0.9714	-0.89
0.5047	108.28	0.9774	0.47
0.6322	105.95	0.9827	1.02
0.6817	104.05	0.9841	-0.09
0.8008	103.30	0.9872	0.57
0.9070	102.05	0.9905	0.39
0.9482	101.52	0.9929	0.35
mean dev			0.84
max dev			2.31

[a] T_{calc} is the bubble-point temperature calculated by using the Wilson model.

Table III. Calculated Activity Coefficients by Using the Wilson Equation for the THF + GBL System

x_{THF}	T/°C	γ_{THF}	γ_{GBL}
0.0276	178.12	1.542	1.000
0.1076	132.15	1.446	1.003
0.2108	111.18	1.390	1.012
0.2997	96.10	1.341	1.028
0.4142	86.55	1.273	1.064
0.4991	82.48	1.221	1.107
0.6044	78.00	1.158	1.189
0.7009	75.12	1.103	1.309
0.8046	71.20	1.052	1.524
0.9047	69.22	1.015	1.900
0.9574	67.08	1.003	2.232

Table IV. Calculated Activity Coefficients by Using the Wilson Equation for the Water + GBL System

x_{water}	T/°C	γ_{water}	γ_{GBL}
0.0612	163.98	1.786	1.001
0.1077	147.90	1.862	1.004
0.2036	125.28	1.860	1.020
0.2913	117.70	1.782	1.049
0.4068	110.50	1.626	1.118
0.5047	108.28	1.489	1.218
0.6322	105.95	1.320	1.445
0.6817	104.05	1.260	1.586
0.8008	103.30	1.131	2.188
0.9070	102.05	1.040	3.647
0.9482	101.52	1.015	5.026

Samples were prepared gravimetrically by weighing the individual components up to fourth decimal accuracy. Care was taken throughout the experimentation to minimize the exposure of THF and GBL to moisture. All the experiments were carried out under a dry nitrogen atmosphere.

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Table V. Wilson Parameters ($J \cdot mol^{-1}$) for the THF + GBL and Water + GBL Systems at 1.013 bar

	$\lambda_{12} - \lambda_{11}$	$\lambda_{12} - \lambda_{22}$
THF + GBL	2884.9145	-88.1321
H_2O + GBL	8781.3525	-1832.6880
THF + H_2O[a]	4775.9577	7617.4777

[a] From ref *4*.

Results and Data Reduction

Experimental T–x data are reported in Tables I and II. Pure component properties have been calculated from the correlations given in part 1 (*2*). Vapor pressures of THF, GBL, and water were taken from ref *7*, *8*, and *9*, respectively. The Wilson model (*10*) has been used to obtain activity coefficients:

$$\ln \gamma_1 = -\ln (x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \quad (1)$$

$$\ln \gamma_2 = -\ln (x_2 + \Lambda_{21}x_1) - x_1\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \quad (2)$$

$$\Lambda_{ij} = \frac{v_j^L}{v_i^L} \exp\left[-\frac{(\lambda_{ij} - \lambda_{ii})}{RT}\right] \quad (3)$$

Wilson equation parameters and vapor-phase mole fractions have been obtained by minimizing the sum of the squares of the deviations in the boiling temperatures for all the data points. Vapor-phase correction has been applied by using the virial equation (*11*). We have used the BUBL T algorithm (*11*) with the Nelder–Mead optimization technique (*12*) for parameter estimation.

Calculated vapor compositions and individual deviations in temperatures are also included in Tables I and II. Calculated activity coefficients using Wilson equation are given in Tables III and IV. Wilson parameters are given in Table V.

Registry No. GBL, 96-48-0; THF, 109-99-9.

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