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Vapor–Liquid Equilibria for the Mixtures Ether + 2-Butanol and + Propyl Acetate at 101.3 kPa

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Vapor–liquid equilibrium data at 101.3 kPa pressure for the systems 2-butanol + dibutyl ether, 2-butanol + tetrahydrofuran, propyl acetate + dibutyl ether, and propyl acetate + tetrahydrofuran are reported. The experimental data were well correlated by different thermodynamic equations. The experimental data have also been compared with those predicted by the UNIFAC group contribution method.

Introduction

Vapor–liquid equilibrium (VLE) data are essential to design a separation process of liquid mixtures of distillation. In our department we have experimentally studied the catalytic esterification of acetic acid with several alcohols using different ethers as azeotropic entrainers (*1*). The separation of the mixtures ether + ester and ether + alcohol is very important because of their influence in the overall yield of the process, ester purity, and recovery of the entrainer.

With this purpose and due to the absence of literature data, isobaric VLE data for the binary mixtures 2-butanol + dibutyl ether, 2-butanol + tetrahydrofuran, propyl acetate + dibutyl ether, and propyl acetate + tetrahydrofuran are reported at 101.3 kPa. The experimental data were correlated by using the van Laar, Wilson, and NRTL equations. The present experimental data along with other data of ether + ester and ether + alcohol mixtures previously reported (*2*) have also been compared with those calculated from the UNIFAC group contribution method.

Experimental Section

Materials. All chemicals (from Merck) were distilled through a column (20-mm i.d. and 900 mm long) packed with 2 × 2 mm Dixon rings, working under an atmosphere of nitrogen. The final purity of all chemicals, estimated by gas–liquid chromatography, was higher than 99.8%. Some physical properties (density, ρ, refractive index, n, and normal boiling point, T_b) are shown in Table 1 and are in good agreement with the literature values (*3*).

Apparatus and Procedure. The VLE data were obtained by use of an all-glass recirculation still connected to a constant-pressure system. The equilibrium temperatures were measured accurate to 0.05 K with a certified PROTON mercury thermometer. The accuracy in the determination of pressure was 101.3 ± 0.1 kPa. Other experimental details have been described previously (*4*).

The liquid and condensed vapor compositions were obtained from density measurements at 298.15 K by using a double leveling pycnometer, except for the system tetrahydrofuran + propyl acetate whose compositions were determined by using a Hewlett-Packard gas chromatograph equipped with a flame ionization detector (the column, 6 ft long and 1/8 in. in diameter, was UCC-10% W 982). Previous calibration analysis was carried out with mixtures of known composition. The molar fractions of the mixtures were estimated to be within ±0.001 accuracy for both phases.

Results

Table 2 presents the experimental VLE data for the previously referred systems at 101.3 kPa, together with the calculated values of the liquid-phase activity coefficients (γ_1 and γ_2).

Table 1. Densities ρ, Refractive Indexes n, and Normal Boiling Points T_b of the Chemicals

	ρ(298.15 K)/(kg m^{-3})		n(D, 298.15 K)		T_b/K	
	exptl	lit.	exptl	lit.	exptl	lit.
2-butanol	0.8028	0.8026	1.3952	1.3950	99.5	99.5
propyl acetate	0.8831	0.88303	1.3824	1.3828	101.5	101.55
dibutyl ether	0.7641	0.7641	1.3968	1.3968	142.1	142.2
tetrahydrofuran	0.8823	0.8822	1.4051	1.4049	66.1	66.2

The activity coefficients, γ_i, in the liquid phase were calculated using the equation

$$\gamma_i = \left(\frac{\phi_i y_i P}{x_i \phi_i^{\circ} P_i^{s}}\right) \exp[(P_i^{s} - P) v_i^{L}/RT]$$

Vapor-phase nonidealities were calculated from the second virial coefficients obtained by the method of Hayden and O'Connell (*5*). The values used for the critical constants, the acentric factors, and the dipole moments were taken from Reid et al. (*6*). Vapor pressures were calculated by use of the Antoine equation with the constants from Riddick et al. (*3*).

The experimental data of the four systems were found to be thermodynamically consistent as checked by using the Herington test (*8*). The systems present area deviations below 3%.

The data were correlated by the van Laar (*9*), Wilson (*10*), and NRTL (*11*) equations. The adjustable binary parameters of each model were estimated by a nonlinear regression method (*12*) that minimizes the following objective function:

$$\sum_{i=1}^{N} [\ln(\gamma_1/\gamma_2)_{i,\mathrm{calcd}} - \ln(\gamma_1/\gamma_2)_{i,\mathrm{exptl}}]^2$$

The resulting parameters from the fit to each model are shown in Table 3, along with the average absolute deviations of the vapor compositions, between the experimental and the fitted values. The results indicate that all equations are suitable to represent the data.

The equilibrium data were predicted by the UNIFAC group contribution method, taking the parameters from the literature (*13*). The mean absolute deviations obtained for the vapor composition in each system were 0.056 for 2-butanol + dibutyl ether, 0.024 for tetrahydrofuran + 2-butanol, 0.048 for tetrahydrofuran + propyl acetate, and 0.019 for propyl acetate + dibutyl ether.

Using the experimental data presented in this work along with other VLE data of binary mixtures ether + alcohol and ether + ester determined previously in our department, new

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Table 2. Experimental VLE Data at 101.3 kPa: Boiling Temperature T, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, and Calculated Activity Coefficients γ_1 and γ_2

T/K	x_1	y_1	γ_1	γ_2
	2-Butanol (1) + Dibutyl Ether (2)			
411.3	0.108	0.098	1.671	1.007
407.3	0.042	0.202	1.643	1.017
401.1	0.093	0.360	1.570	1.022
397.7	0.131	0.440	1.502	1.029
393.8	0.190	0.531	1.403	1.036
391.2	0.234	0.584	1.356	1.005
386.9	0.328	0.675	1.278	1.065
383.6	0.425	0.740	1.202	1.104
380.2	0.566	0.812	1.107	1.178
377.6	0.681	0.861	1.065	1.289
376.1	0.768	0.900	1.039	1.340
374.4	0.875	0.944	1.015	1.474
373.5	0.935	0.970	1.007	1.565
373.0	0.975	0.989	1.002	1.517
	Tetrahydrofuran (1) + 2-Butanol (2)			
369.5	0.078	0.205	1.145	0.970
366.8	0.140	0.322	1.072	0.983
363.1	0.209	0.432	1.059	1.035
361.1	0.274	0.527	1.038	1.016
359.7	0.321	0.589	1.027	0.999
357.3	0.385	0.661	1.024	1.004
356.3	0.421	0.700	1.019	0.984
354.1	0.487	0.756	1.010	0.990
350.9	0.588	0.826	0.998	1.008
347.9	0.658	0.864	1.015	1.083
344.5	0.787	0.927	1.004	1.087
342.7	0.859	0.951	0.995	1.197
340.9	0.917	0.974	1.006	1.173
	Propyl Acetate (1) + Dibutyl Ether (2)			
411.5	0.036	0.109	1.171	1.008
406.7	0.095	0.256	1.164	1.020
404.9	0.124	0.338	1.123	1.001
401.3	0.181	0.417	1.131	1.026
398.5	0.238	0.498	1.100	1.028
395.3	0.299	0.575	1.095	1.038
392.3	0.368	0.650	1.086	1.036
388.9	0.457	0.727	1.069	1.042
384.6	0.587	0.815	1.047	1.060
383.1	0.648	0.849	1.029	1.064
380.7	0.734	0.893	1.021	1.077
378.4	0.828	0.934	1.011	1.106
377.1	0.888	0.957	1.002	1.155
375.6	0.949	0.980	1.003	1.239
	Tetrahydrofuran (1) + Propyl Acetate (2)			
370.5	0.304	0.124	1.611	1.023
366.9	0.076	0.254	1.606	1.017
364.3	0.111	0.338	1.558	1.017
362.0	0.147	0.407	1.498	1.021
359.7	0.185	0.469	1.453	1.031
356.5	0.250	0.556	1.382	1.041
353.6	0.348	0.641	1.235	1.068
351.5	0.409	0.694	1.202	1.080
349.0	0.498	0.744	1.131	1.160
347.8	0.550	0.770	1.096	1.213
345.0	0.681	0.843	1.046	1.293
343.7	0.752	0.877	1.022	1.366
342.5	0.808	0.906	1.017	1.410
341.2	0.895	0.949	0.998	1.469

Table 3. Fitted Parameters and Mean Deviations in the Vapor Phase from Data Correlation

parameter	propyl acetate (1) + dibutyl ether (2)	2-butanol (1) + dibutyl ether (2)	tetrahydrofuran (1) + 2-butanol (2)	tetrahydrofuran (1) + propyl acetate
		van Laar Equation		
A	0.1272	0.5237	0.0669	0.4896
B	0.3805	0.5959	0.0782	0.5820
MDV	0.0025	0.0019	0.0039	0.0053
		Wilson Equation		
Λ_{12}	1.0722	0.7530	1.1023	0.6554
Λ_{12}	0.7655	0.7635	0.8358	0.8872
MDV	0.0028	0.0019	0.0039	0.0053
		NRTL Equation ($\alpha_{12} = 0.47$)		
G_{12}	0.0781	0.3244	0.1971	0.3048
G_{12}	0.0907	0.2602	−0.1127	0.3386
MDV	0.0032	0.0019	0.0039	0.0053

UNIFAC parameters were calculated (*14*). The results of the predictions were (mean deviation in the vapor compositions) 0.018 for 2-butanol + dibutyl ether, 0.013 for tetrahydrofuran + 2-butanol, 0.050 for tetrahydrofuran + propyl acetate, and 0.008 for propyl acetate + dibutyl ether.

Taking into account the observed differences, these parameters cannot be recommended as definitive values for VLE predictions. Therefore, it is necessary to increase the data base in order to determine more accurate UNIFAC parameters.

Glossary

MDV	average absolute deviation of the vapor composition, $\sum\lvert(y_{\text{exptl}} - y_{\text{calcd}})_i\rvert/N$
N	number of data points
P	total pressure
P_i^{s}	vapor pressure of pure component i
T	temperature
v_i^{L}	molar liquid volume of component i
x_i	liquid mole fraction of component i
y_i	vapor mole fraction of component i
α_{ij}	NRTL nonrandomness parameter
ϕ_i	vapor-phase fugacity coefficient of component i
ϕ_i^{s}	vapor-phase fugacity coefficient of pure saturated vapor i
γ_i	liquid-phase activity coefficient of component i

Registry Numbers Supplied by Author. 2-Butanol, 78-92-2; propyl acetate, 109-60-4; dibutyl ether, 142-96-1; tetrahydrofuran, 109-99-9.

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