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Vapor–Liquid Equilibria of Coal-Derived Liquids. 3. Binary Systems with Tetralin at 200 mmHg

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Isobaric vapor–liquid equilibrium data are reported for binary systems of tetralin with *p*-xylene, γ-picoline, piperidine, and pyridine; all systems were measured at 26.66 kPa (200 mmHg) with a recirculation still. Liquid-phase activity coefficients were correlated using the Van Laar, Wilson, NRTL, and UNIQUAC equations. Vapor-phase nonidealities were found negligible under the experimental conditions of this work, and deviations of the liquid phase from the ideal behavior, as described by Raoult's law, were found to be slightly positive for all the systems.

Introduction

Chemicals obtained by coal liquefaction and gasification cannot compete at present with petroleum-derived products. However, there is a permanent interest in the use of coal or coal heavy fractions from coking operations, to produce liquid fuels and feedstocks for the petrochemical industry (*1, 2*). Hydroaromatic compounds, such as tetralin, are widely used as solvents in carbochemical processes, mainly as extractants and in hydrogenation reactions. Tetralin acts as a hydrogen donor molecule, hydrogen being transferred from the hydroaromatic compound to a compound that readily accepts hydrogen.

The design of separation processes involving complex mixtures of coal-derived fluids requires reliable vapor–liquid equilibrium (VLE) data, and several publications on the subject have appeared in recent years (*3–9*).

Following earlier works on isobaric VLE of binary mixtures of coal-derived liquids (*10, 11*), data are presented in this work on VLE for binary systems containing tetralin and one aromatic heterocycle (pyridine and γ-picoline), tetralin and one nonaromatic heterocycle (piperidine), and tetralin and one aromatic hydrocarbon (*p*-xylene). No literature data exist for the systems studied. Data are reported at 26.66 kPa (200 mmHg), and have been checked for thermodynamic consistency and correlated with the following models: Van Laar, Wilson, NRTL, and UNIQUAC.

Experimental Section

A. Chemicals. All the chemicals, tetralin (>97%, GC), *p*-xylene (>99%, GC), γ-picoline (>98%, GC), pyridine (>99.8%, GC), and piperidine (>99%, GC) were supplied by Fluka. Tetralin and γ-picoline were purified in a distillation column at reduced pressure (2.67 and 8.00 kPa, respectively). The middle fraction was collected, and stored under nitrogen in the dark. The other chemicals were used without further purification. Product purity was checked by gas chromatography. Physical properties for the liquids used are reported in Table 1, both experimental and values found in the literature (*12*).

B. Apparatus and Procedure. The still used to measure VLE data was an all-glass still of the Gillespie type (*13*) as modified by Röck et al. (*14*). It is a commercial unit manufactured by Fritz GmbH (Normag) Hofheim (Germany) and has been previously described (*15*).

Table 1. Density ρ, Refractive Index n, and Boiling Point T_b of the Compounds

	ρ(298.15 K)/(kg m^{-3})		n(D,293.15 K)		n(D,298.15 K)		T_b(26.66 kPa)/K
compound	exptl	lit. (*12*)	exptl	lit. (*12*)	exptl	lit. (*12*)	exptl
p-xylene	856.4	856.61			1.4930	1.493 25	367.85
γ-picoline	950.5	950.20			1.5029	1.503 22	375.10
piperidine	854.2	856.64	1.4522	1.452 50	1.4502		339.70
pyridine	978.4	978.24			1.5077	1.507 45	348.20
tetralin	966.0	966.00			1.5392	1.539 19	430.15

Table 2. Refractive Indexes n(D,298.15 K) for the Binary Systems γ-Picoline (1) + Tetralin (2), Piperidine (1) + Tetralin (2), and Pyridine (1) + Tetralin (2) as a Function of the Mole Fraction x_1

γ-picoline (1) + tetralin (2)		piperidine (1) + tetralin (2)		pyridine (1) + tetralin (2)	
x_1	n	x_1	n	x_1	n
0.1051	1.5361	0.1129	1.5312	0.1318	1.5378
0.1437	1.5351	0.2129	1.5241	0.2332	1.5350
0.2796	1.5310	0.3043	1.5171	0.3064	1.5330
0.3525	1.5283	0.4540	1.5049	0.4358	1.5299
0.5600	1.5210	0.5628	1.4956	0.5380	1.5269
0.6389	1.5181	0.6777	1.4848	0.6389	1.5239
0.7614	1.5131	0.7758	1.4753	0.7251	1.5204
0.8570	1.5091	0.8155	1.4710	0.8048	1.5173
0.9117	1.5066	0.9184	1.4596	0.8753	1.5147
				0.9380	1.5116

Table 3. Density ρ for the Binary System *p*-Xylene (1) + Tetralin (2) as a Function of the Mole Fraction x_1 of *p*-Xylene

x_1	ρ(298.15 K)/(kg m^{-3})	x_1	ρ(298.15 K)/(kg m^{-3})
0.1885	946.4	0.6302	900.9
0.2471	941.2	0.7283	888.2
0.3353	931.8	0.8314	876.7
0.4215	923.4	0.8959	868.5
0.5243	911.7		

Experiments were started by filling the equilibrium still with dried nitrogen before loading the system under investigation. The equipment was then started, the operation conditions were set, and the steady-state was reached. The system was allowed to recirculate for about 1 h under steady-

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Table 4. Experimental Vapor Pressure Data, Temperature T and Pressure P, for p-Xylene, γ-Picoline, Piperidine, Pyridine, and Tetralin

p-xylene		γ-picoline		piperidine		pyridine		tetralin	
T/K	P/kPa	T/K	P/kPa	T/K	P/kPa	T/K	P/kPa	T/K	P/kPa
366.60	25.29	374.70	26.34	339.35	26.44	345.45	23.89	419.40	18.99
367.85	26.66	375.10	26.66	339.70	26.66	347.20	25.54	423.35	21.62
368.10	26.82	378.25	29.74	344.50	32.17	348.20	26.66	424.85	22.59
370.60	29.29	381.15	32.81	350.25	39.57	349.60	28.02	430.15	26.66
373.05	31.79	383.70	35.82	352.50	42.84	351.65	30.09	430.30	26.73
373.45	32.22	391.90	46.77	354.90	46.61	353.55	32.35	434.60	30.37
375.85	34.86	399.45	59.38	357.50	50.75	355.05	34.14	437.55	33.17
377.90	37.49			359.05	53.55	356.75	36.27	439.75	35.40
				360.55	56.22	359.40	39.87		
						362.50	44.26		

Table 5. Fitted Antoine Equation[a] Parameters A, B, and C and Correlation Coefficient R^2

compound	A	B	C	R^2
p-xylene	7.982 92	2081.185	271.461	0.999 27
γ-picoline	8.473 03	2520.009	306.313	0.999 95
piperidine	7.058 35	1365.675	220.691	0.999 96
pyridine	7.751 31	1834.779	261.478	0.999 91
tetralin	7.296 86	1893.766	221.986	0.999 94

[a] Antoine equation: $\log(P/\mathrm{mmHg}) = A - B/[(t/°\mathrm{C}) + C]$.

Table 6. Vapor–Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature T, and Activity Coefficients γ_i, Equation 1, for p-Xylene (1) + Tetralin (2) at 26.66 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	430.15		1.003
0.038	0.215	424.25	1.000	0.979
0.103	0.475	414.65	1.051	0.958
0.217	0.677	403.75	0.974	0.979
0.315	0.790	395.45	1.007	0.980
0.437	0.860	389.35	0.957	0.999
0.477	0.877	386.25	0.987	1.065
0.502	0.895	384.85	1.002	1.008
0.530	0.908	383.60	1.003	0.983
0.597	0.923	380.75	0.995	1.075
0.690	0.957	377.35	1.001	0.896
0.795	0.973	373.75	0.999	0.987
1.000	1.000	367.85	1.004	

Table 7. Vapor–Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature T, and Activity Coefficients γ_i, Equation 1, for γ-Picoline (1) + Tetralin (2) at 26.66 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	430.15		1.003
0.125	0.477	412.85	1.147	1.039
0.192	0.602	406.95	1.122	1.046
0.217	0.637	405.10	1.111	1.049
0.277	0.720	400.55	1.130	1.029
0.320	0.762	398.10	1.117	1.016
0.360	0.794	396.05	1.103	1.007
0.405	0.812	393.60	1.084	1.082
0.440	0.840	391.75	1.095	1.048
0.490	0.867	389.85	1.079	1.028
0.530	0.890	388.15	1.082	0.984
0.585	0.907	385.85	1.078	1.030
0.630	0.922	384.65	1.059	1.016
0.690	0.935	382.65	1.048	1.093
0.758	0.957	380.65	1.045	1.003
0.850	0.972	378.95	1.003	1.129
0.917	0.987	376.65	1.021	1.041
1.000	1.000	375.10	1.001	

Table 8. Vapor–Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature T, and Activity Coefficients γ_i, Equation 1, for Piperidine (1) + Tetralin (2) at 26.66 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	430.15		1.003
0.075	0.663	398.75	1.358	1.033
0.108	0.724	394.05	1.167	1.042
0.128	0.777	389.40	1.200	1.025
0.170	0.822	384.50	1.097	1.039
0.215	0.868	378.35	1.095	1.042
0.295	0.923	369.35	1.116	0.987
0.353	0.942	365.65	1.070	0.952
0.462	0.960	358.25	1.063	1.102
0.545	0.965	354.50	1.029	1.359
0.605	0.980	351.90	1.030	1.013
0.705	0.987	348.05	1.021	1.064
0.792	0.992	345.50	1.002	1.055
0.852	0.994	343.05	1.022	1.259
0.960	0.998	340.75	0.992	1.749
1.000	1.000	339.70	0.995	

state conditions before withdrawing samples of both phases for analysis.

The boiling point temperature in the equilibrium still was measured with a mercury-in-glass thermometer (0.01 K divisions) calibrated against a standard thermometer. Experimental runs were carried out at 26.66 kPa. The atmospheric pressure was measured with a standard barometer. Nitrogen was injected or released to adjust the pressure in the equilibrium still to 26.66 ± 0.03 kPa as indicated by a mercury manometer.

Both vapor- and liquid-phase compositions were determined by gas–liquid chromatography (Perkin-Elmer, model 990, flame ionization detector) and refractometry (Abbe-type refractometer, 0.0002 division) or pycnometry (absolute error 0.0002), two methods always being used for the analysis of each sample. No significant difference in composition was found between them; standard deviations of compositions were 0.005. The chromatographic column (3 m × 0.3 cm) was packed with 15% Carbowax 1500 on Chromosorb WHP 60/80 mesh. Chromatographic analysis was carried out at the following column temperatures: systems with p-xylene and piperidine at 398.15 K, the system with γ-picoline at 393.15 K, and the system with pyridine at 403.15 K.

Results and Discussion

Refractive indexes n_D at 298.15 K for the binary mixtures γ-picoline (1) + tetralin (2), piperidine (1) + tetralin (2), and pyridine (1) + tetralin (2) are reported in Table 2. Table 3 shows the densities ρ at 298.15 K for the binary mixture p-xylene (1) + tetralin (2). In Table 4 experimental temperature–pressure data for the pure compounds are listed. These experimental data were used to determine the parameters for the Antoine equation used in the VLE data regression, and are reported in Table 5.

The experimental VLE data, i.e., vapor- and liquid-phase compositions, temperature, and pressure (26.66 kPa), for the binary systems under study, p-xylene (1) + tetralin (2), γ-picoline (1) + tetralin (2), piperidine (1) + tetralin (2), and pyridine (1) + tetralin (2), are reported in Tables 6-9, together with the activity coefficients calculated from experimental data for each system. Figure 1 shows the y–x diagrams where

Table 9. Vapor–Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature T, and Activity Coefficients γ_i, Equation 1, for Pyridine (1) + Tetralin (2) at 26.66 kPa

x_1	y_1	T/K	γ_1	γ_2
0.000	0.000	430.15		1.003
0.025	0.332	417.85	1.549	1.010
0.030	0.348	416.65	1.395	1.048
0.050	0.494	411.30	1.366	0.975
0.160	0.795	389.85	1.252	0.962
0.196	0.840	385.00	1.248	0.946
0.237	0.873	380.90	1.216	0.931
0.287	0.900	376.70	1.181	0.930
0.378	0.932	369.55	1.170	0.979
0.495	0.955	364.10	1.099	1.013
0.575	0.967	360.50	1.084	1.038
0.664	0.977	357.70	1.046	1.041
0.720	0.982	355.55	1.047	1.081
0.830	0.988	352.55	1.018	1.369
0.882	0.992	351.05	1.017	1.414
0.926	0.995	350.05	1.007	1.479
0.963	0.996	349.30	0.997	2.455
0.980	0.998	348.85	0.998	2.322
1.000	1.000	348.20	1.004	

experimental data and data calculated by the UNIQUAC equation have been plotted for comparison.

Vapor-phase fugacity coefficients were calculated using the virial equation of state (*16*), where the second virial coefficients were estimated by the Hayden and O'Connell correlation (*17*). Fugacity coefficients estimated by this method lie between 1.00 (ideal) and 0.98 (nearly ideal). Thus, vapor-phase nonideality was not used in the reduction of data for the correlation of liquid-phase nonideality. The Poynting correction was considered equal to 1 for the experimental conditions in this work. Liquid-phase activity coefficients, γ_i, were thus calculated by the equation

$$\gamma_i = y_i P / x_i P_i^s \qquad (1)$$

where y_i are the vapor-phase mole fractions, P is the total pressure, γ_i are the activity coefficients of the components, and x_i are the liquid-phase mole fractions. Vapor pressures of pure components P_i^s were calculated with the parameters of the Antoine equation obtained from the regression of the experimental temperature–pressure data for the pure components.

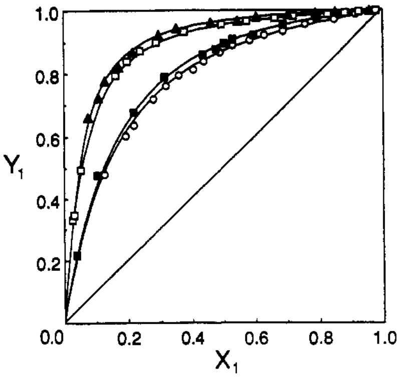

Figure 1. x–y diagram for the binary systems (■) p-xylene (1) + tetralin (2), (○) γ-picoline (1) + tetralin (2), (▲) piperidine (1) + tetralin (2), and (□) pyridine (1) + tetralin (2). Continuous lines represent data calculated with the UNIQUAC correlation equation for the four sets of data.

Experimental VLE data were correlated by the Van Laar (*18*, *19*), Wilson (*20*), NRTL (*21*), and UNIQUAC (*22*) equations. These equations contain two adjustable binary parameters which were estimated by a nonlinear regression method based on the maximum-likelihood principle (*23*). This regression procedure weighs each individual measurement according to experimental uncertainty. The parameter α_{12} in the NRTL equation was kept constant; $\alpha_{12} = 0.3$ in all cases. The adjustable parameters A_{12} and A_{21} for the correlation equations together with infinite dilution activity coefficients, and root-mean-squared deviations for pressure, temperature, and vapor- and liquid-phase compositions, are listed in Table 10. None of the systems studied are highly nonideal. Thus, all the equations, including the equation of Van Laar, yield a similar fit for the experimental data.

Small positive deviations from Raoult's law are due to slightly stronger interactions among like molecules than among the unlike ones. π–π interactions among like p-xylene molecules, N–HN interactions among like piperidine molecules, the rather strong dipole–dipole interactions, μ(pyridine) = 2.37 and μ(γ-picoline) = 2.6, and π–π interactions among like pyridine bases have a compensation effect for the π–π, NH–π, and dipole–induced dipole (μ–π) interactions, of

Table 10. Correlation Parameters A_{12}, A_{21}, and α_{12} for Activity Coefficient Models, Root-Mean-Squared Deviations, and Activity Coefficients at Infinite Dilution γ_i^∞

						root-mean-squared deviations			
	A_{12}	A_{21}	α_{12}	γ_1^∞	γ_2^∞	P/kPa	T/K	x_1	y_1
p-Xylene (1) + Tetralin (2)									
Van Laar	−0.03	−0.03		0.970	0.970	0.25	0.03	0.0017	0.0074
Wilson	5.10	−26.23		0.972	0.969	0.25	0.03	0.0017	0.0074
NRTL[a]	91.12	−111.73	0.30	0.989	0.989	0.25	0.03	0.0017	0.0074
UNIQUAC[a]	−50.04	48.31		0.960	0.960	0.25	0.03	0.0017	0.0075
γ-Picoline (1) + Tetralin (2)									
Van Laar	0.15	0.40		1.162	1.492	0.20	0.03	0.0005	0.0062
Wilson	−116.98	507.03		1.127	1.349	0.20	0.03	0.0005	0.0063
NRTL[a]	953.90	−552.31	0.30	1.253	1.641	0.21	0.03	0.0005	0.0064
UNIQUAC[a]	128.15	−75.45		1.124	1.194	0.21	0.03	0.0005	0.0062
Piperidine (1) + Tetralin (2)									
Van Laar	0.27	0.15		1.310	1.162	0.33	0.04	0.0023	0.0045
Wilson	696.67	−473.90		1.594	1.373	0.33	0.04	0.0024	0.0044
NRTL[a]	−334.83	570.17	0.30	1.096	1.051	0.33	0.04	0.0024	0.0044
UNIQUAC[a]	−132.93	185.54		1.015	1.023	0.33	0.04	0.0024	0.0045
Pyridine (1) + Tetralin (2)									
Van Laar	0.29	0.40		1.336	1.492	0.22	0.03	0.0012	0.0054
Wilson	401.02	−115.90		1.392	1.555	0.23	0.03	0.0014	0.0055
NRTL[a]	441.34	−142.90	0.30	1.433	1.587	0.22	0.03	0.0013	0.0055
UNIQUAC[a]	−84.15	178.14		1.015	1.031	0.23	0.03	0.0014	0.0055

[a] A_{12} and A_{21} are in calories per mole.

p-xylene, piperidine, and pyridine bases, respectively, with the π-electrons of tetralin resulting in positive deviations in all cases. The higher the energetic difference between the interactions among like and unlike molecules, the larger the deviation from ideality. Hence, nearly ideal behavior should be expected for the *p*-xylene + tetralin system. In fact, activity coefficients for this system (Table 6) lie between 0.95 and 1.07. Liquid-phase deviations from ideal behavior are considered to be within experimental uncertainty.

Separation of the components in the mixtures studied, by simple or fractional distillation, should not present any difficulties, as could be concluded from the *x*–*y* diagrams in Figure 1.

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Registry Numbers Supplied by the Author. Tetralin, 119-64-2; γ-picoline, 108-89-4; Pyridine, 110-86-1; Piperidine, 110-89-4; p-Xylene, 106-42-3.

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