Vapor–Liquid Equilibria and Excess Gibbs Energies for Binary Systems of Pyridine Base with Hydrocarbons at 313.15 K

Stanisław Warycha

Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland

Results of total vapor pressure measurements, performed at 313.15 K by a static method, are reported for 12 binary systems formed by pyridine + heptane, + octane, or + nonane, 2-picoline + benzene, + toluene, + heptane, + octane, or + nonane, 3-picoline + benzene or + toluene, and 4-picoline + benzene or + toluene. The results were correlated by using the Wilson equation. Calculated parameters of azeotropic points are also reported.

Introduction

This investigation is part of a research project consisting of the experimental determination of vapor–liquid equilibria (VLE) for binary mixtures of selected solvents at a constant temperature. For technical reasons the temperature 313.15 K was chosen. In previous papers (*1*, *2*) a considerable amount of VLE data for binary systems of the type pyridine base + aliphatic alcohol has been published by the author of this paper. Studies on the self-association of pyridine bases in isooctane have also been published (*3*, *4*). This paper reports the results of VLE measurements for 12 systems of pyridine base (pyridine and isomeric picolines) with hydrocarbons.

Table I. Minimum Mole Fraction of the Main Component x, Maximum Mole Fraction of Water x_w, Vapor Pressure $P_i°$, Second Molar Virial Coefficient β_{ii}, and Liquid Molar Volume $V_i°$ at 313.15 K

			$P_i°$/kPa			
compound	10^2x	10^2x_w	this work	lit.	$-\beta_{ii}$/(dm^3 mol^{-1})	$V_i°$/(dm^3 mol^{-1})
benzene	99.9	0.03	24.371	24.366 (*6*)	1.426	0.094
toluene	99.9	0.04	7.890	7.887 (*6*)	2.276	0.109
heptane	99.9	0.02	12.318	12.324 (*6*)	2.555	0.154
octane	99.8	0.05	4.133	4.140 (*6*)	3.765	0.169
nonane	99.8	0.04	1.149	1.403 (*6*)	5.338	0.189
pyridine	99.9	0.03	6.040	6.016 (*5*)	2.817	0.092
2-picoline	99.8	0.04	3.432	3.398 (*5*)	3.372	0.098
3-picoline	99.8	0.04	1.933	1.887 (*5*)	3.683	0.102
4-picoline	99.8	0.05	1.828	1.803 (*5*)	3.741	0.102

Experimental Section

Materials. Benzene and pyridine and its derivatives (Merck) were twice crystallized, dried over NaOH, and fractionated on an efficient column having 80 theoretical plates. The remaining hydrocarbons (analytical reagent grade, POCh) were fractionally distilled. The fractions distilling within a 0.01 K range were used. The purities were checked chromatographically, and the water content was determined by Fischer's reagent. Table I gives the purities, the measured vapor pressures compared to literature values $P_i°$, the second virial coefficients β_{ii}, and the liquid molar volumes $V_i°$ of the components. The cross virial coefficients β_{ij} are reported in Table III. The literature vapor pressures of the pyridines have been calculated from the Antoine constants given by Herington and Martin (*5*). These constants, however, were determined from pressure values at temperatures higher by about 30 K than the temperature used in this investigation. The systematic discrepancies may be attributed to this circumstance.

Apparatus and Procedure. Vapor–liquid equilibrium data were obtained with a static equilibrium apparatus. Details of

Table II. Vapor–Liquid Equilibrium Data for the Binary Systems at 313.15 K: Experimental Liquid Mole Fraction x_1, Total Vapor Pressure P, and Calculated Vapor Mole Fraction y_1

x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa
2-Picoline (1) + Benzene (2)											
0.0000	0.0000	24.371	0.2204	0.0404	19.941	0.5336	0.1386	13.466	0.7707	0.3145	8.455
0.0122	0.0019	24.114	0.3524	0.0731	17.216	0.6069	0.1769	11.918	0.8367	0.4099	7.073
0.0922	0.0154	22.557	0.4118	0.0912	15.928	0.6722	0.2206	10.564	0.9001	0.5484	5.706
0.1622	0.0284	21.089	0.4870	0.1185	14.417	0.7253	0.2659	9.450	1.0000	1.0000	3.432
2-Picoline (1) + Toluene (2)											
0.0000	0.0000	7.890	0.3116	0.1714	6.745	0.6139	0.3957	5.422	0.8519	0.6925	4.244
0.0620	0.0337	7.658	0.3759	0.2113	6.479	0.6640	0.4456	5.174	0.8866	0.7526	4.061
0.1475	0.0794	7.338	0.4360	0.2516	6.211	0.7239	0.5127	4.874	1.0000	1.0000	3.432
0.2059	0.1110	7.138	0.4918	0.2922	5.958	0.7266	0.5159	4.885			
0.2610	0.1418	6.950	0.5457	0.3352	5.708	0.7914	0.6003	4.550			
2-Picoline (1) + Heptane (2)											
0.0000	0.0000	12.318	0.2935	0.1597	11.420	0.6009	0.2557	9.913	0.8925	0.4722	6.613
0.0521	0.0419	12.218	0.3516	0.1789	11.196	0.6547	0.2758	9.547	0.9498	0.6321	5.165
0.1295	0.0899	11.984	0.4143	0.1981	10.932	0.7178	0.3044	9.058	1.0000	1.0000	3.432
0.1762	0.1131	11.830	0.4792	0.2174	10.635	0.7781	0.3409	8.422			
0.2388	0.1396	11.622	0.5355	0.2344	10.312	0.8346	0.3903	7.699			
2-Picoline (1) + Octane (2)											
0.0000	0.0000	4.133	0.2942	0.3646	4.988	0.6005	0.5154	5.028	0.8976	0.7259	4.316
0.0675	0.1345	4.486	0.3643	0.4061	5.036	0.6579	0.5415	4.985	0.9527	0.8320	3.941
0.1160	0.2041	4.645	0.4152	0.4323	5.061	0.7238	0.5751	4.897	1.0000	1.0000	3.432
0.1799	0.2746	4.822	0.4827	0.4639	5.084	0.7800	0.6097	4.768			
0.2422	0.3280	4.924	0.5317	0.4855	5.073	0.8422	0.6602	4.568			

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Table II (Continued)

x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa
					2-Picoline (1) + Nonane (2)						
0.0000	0.0000	1.419	0.3553	0.6622	3.040	0.6625	0.7806	3.492	0.9569	0.9384	3.502
0.1274	0.4399	2.252	0.4220	0.6948	3.198	0.7226	0.8008	3.528	1.0000	1.0000	3.432
0.1878	0.5282	2.520	0.4848	0.7204	3.253	0.7780	0.8216	3.542			
0.2369	0.5793	2.686	0.5490	0.7434	3.362	0.8423	0.8509	3.557			
0.3079	0.6339	2.937	0.6016	0.7608	3.429	0.8990	0.8857	3.545			
					3-Picoline (1) + Benzene (2)						
0.0000	0.0000	24.371	0.2965	0.0335	18.004	0.6050	0.1062	11.158	0.8990	0.4035	4.340
0.0552	0.0053	23.197	0.3577	0.0431	16.660	0.6663	0.1334	9.746	0.9520	0.6007	3.118
0.0953	0.0093	22.351	0.4161	0.0538	15.360	0.7262	0.1691	8.373	1.0000	1.0000	1.933
0.1832	0.0188	20.449	0.4809	0.0681	13.926	0.7630	0.1976	7.525			
0.2314	0.0246	19.436	0.5443	0.0853	12.476	0.8308	0.2723	5.940			
					3-Picoline (1) + Toluene (2)						
0.0000	0.0000	7.890	0.3173	0.1070	6.237	0.5503	0.2220	4.894	0.8387	0.5301	3.069
0.0584	0.0192	7.579	0.3883	0.1363	5.872	0.6294	0.2788	4.437	0.9106	0.6858	2.569
0.1514	0.0490	7.129	0.4434	0.1620	5.565	0.6771	0.3203	4.153	1.0000	1.0000	1.933
0.2052	0.0667	6.839	0.5003	0.1919	5.200	0.7267	0.3712	3.830			
0.2586	0.0852	6.578	0.5258	0.2068	5.080	0.7864	0.4466	3.430			
					4-Picoline (1) + Benzene (2)						
0.0000	0.0000	24.371	0.3533	0.0406	16.691	0.6629	0.1246	9.853	0.9510	0.5754	3.028
0.1137	0.0108	21.902	0.4161	0.0515	15.443	0.7283	0.1611	8.349	1.0000	1.0000	1.828
0.1755	0.0173	20.574	0.4868	0.0663	13.764	0.7651	0.1885	7.485			
0.2358	0.0243	19.306	0.5464	0.0817	12.564	0.8322	0.2596	5.865			
0.2940	0.0318	18.005	0.6046	0.1005	11.191	0.9028	0.3945	4.197			
					4-Picoline (1) + Toluene (2)						
0.0000	0.0000	7.890	0.3174	0.1029	6.226	0.6187	0.2587	4.464	0.9136	0.6771	2.486
0.0761	0.0238	7.491	0.3758	0.1257	5.904	0.6673	0.2980	4.158	0.9502	0.7897	2.216
0.1585	0.0493	7.077	0.4386	0.1531	5.544	0.7428	0.3741	3.673	1.0000	1.0000	1.828
0.1985	0.0620	6.877	0.4943	0.1807	5.214	0.7905	0.4353	3.342			
0.2519	0.0797	6.570	0.5515	0.2133	4.878	0.8496	0.5320	2.940			
					Pyridine (1) + Heptane (2)						
0.0000	0.0000	12.318	0.3040	0.2862	13.754	0.6048	0.3696	13.262	0.9039	0.5417	10.327
0.0652	0.1162	13.099	0.3311	0.2960	13.754	0.6606	0.3847	13.063	0.9537	0.6673	8.610
0.1157	0.1735	13.422	0.4242	0.3245	13.671	0.7255	0.4057	12.722	1.0000	1.0000	6.040
0.1654	0.2144	13.627	0.4900	0.3414	13.536	0.7721	0.4253	12.391			
0.2457	0.2612	13.752	0.5355	0.3526	13.428	0.8418	0.4690	11.598			
					Pyridine (1) + Octane (2)						
0.0000	0.0000	4.133	0.2558	0.5183	7.022	0.5334	0.6264	7.650	0.9005	0.7696	7.238
0.0577	0.2468	5.106	0.3575	0.5706	7.390	0.5432	0.6289	7.659	1.0000	1.0000	6.040
0.1131	0.3692	5.910	0.4084	0.5897	7.503	0.6640	0.6593	7.699			
0.1792	0.4559	6.549	0.4228	0.5945	7.531	0.8342	0.7200	7.507			
					Pyridine (1) + Nonane (2)						
0.0000	0.0000	1.419	0.2950	0.7748	5.004	0.5947	0.8423	5.886	0.9051	0.9078	6.175
0.0568	0.4739	2.512	0.3585	0.7963	5.313	0.6574	0.8513	5.980	0.9584	0.9437	6.137
0.1229	0.6394	3.490	0.4197	0.8118	5.536	0.7254	0.8614	6.058	1.0000	1.0000	6.040
0.1456	0.6707	3.781	0.4704	0.8222	5.673	0.7798	0.8708	6.095			
0.2469	0.7526	4.702	0.5457	0.8350	5.810	0.8424	0.8851	6.151			

Table III. Coefficients Λ_{ij} of the Wilson Equation (Equation 1), Standard Deviations $\sigma(\Lambda_{ij})$, Correlation Coefficient q for the Pair (Λ_{12}, Λ_{21}), Absolute, $\sigma(P)^a$, and Relative, $\sigma_r(P)^b$, Standard Deviations of the Total Vapor Pressure, and Cross Molar Second Virial Coefficients β_{ij}

system	Λ_{12}	$\sigma(\Lambda_{12})$	Λ_{21}	$\sigma(\Lambda_{21})$	q	$\sigma(P)$/kPa	$\sigma_r(P)$	$-\beta_{ij}$/(dm^3 mol^{-1})
2-picoline								
+ benzene	1.329 58	0.121 29	0.647 94	0.083 45	−0.9993	0.044	0.39	1.489
+ toluene	1.415 28	0.052 42	0.517 53	0.031 62	−0.9979	0.014	0.24	1.865
+ heptane	0.432 29	0.004 99	0.545 16	0.004 97	−0.9478	0.021	0.24	1.974
+ octane	0.342 77	0.008 77	0.653 23	0.011 21	−0.9683	0.015	0.32	2.392
+ nonane	0.305 38	0.010 36	0.722 43	0.016 12	−0.9618	0.014	0.46	2.834
3-picoline								
+ benzene	1.628 72	0.044 88	0.451 73	0.023 04	−0.9964	0.034	0.50	1.544
+ toluene	1.495 91	0.043 05	0.443 12	0.023 00	−0.9958	0.015	0.29	1.934
4-picoline								
+ benzene	1.463 90	0.054 49	0.528 24	0.031 85	−0.9974	0.037	0.28	1.553
+toluene	1.395 56	0.034 94	0.486 63	0.020 14	−0.9956	0.012	0.32	1.947
pyridine								
+ heptane	0.262 73	0.005 76	0.436 06	0.006 67	−0.9129	0.053	0.46	1.804
+ octane	0.217 03	0.010 14	0.503 89	0.013 57	−0.9386	0.040	0.70	2.190
+ nonane	0.191 97	0.005 93	0.547 73	0.009 59	−0.8907	0.030	0.73	2.601

^{a} $\sigma(P) = \sum[(P_{exptl} - P_{calcd})^2/(m-n)]^{0.5}$, where n is the number of parameters and m is the number of experimental points. ^{b} $\sigma_r(P) = 100\sum[(1 - P_{calcd}/P_{exptl})^2/(m-n)]^{0.5}$, where n is the number of parameters and m is the number of experimental points.

the apparatus are given elsewhere (7). The apparatus works without a null manometer, and degassing of the sample is done without freezing. The volume of the sample was about 2.5 cm^3. During measurements the temperature was constant to within

Table IV. Mole Fractions x_{1az} and Pressures P_{az} of Azeotropic Mixtures

system	x_{1az}	P_{az}/kPa
2-picoline (1) + octane (2)	0.448	5.07
2-picoline (1) + nonane (2)	0.862	3.56
pyridine (1) + heptane (2)	0.274	13.81
pyridine (1) + octane (2)	0.658	7.69
pyridine (1) + nonane (2)	0.911	6.21

0.004 K and was controlled up to 0.002 K; the absolute deviation was estimated to be equal to ±0.02 K (IPTS-68). The cathetometer readings contribute less than 0.004 kPa to the error of a single pressure measurement. This is a major part of the error in pressure if both errors in temperature and pressure are treated separately. The errors in the liquid mole fractions were less than 0.0005.

Results and Discussion

The results of total vapor pressure P measurements are given in Table II as a function of the mole fraction x of the pyridine base. The experimental (x, P) data were correlated by several commonly used excess molar Gibbs energy G^E equations, e.g., Wilson (*8*). Redlich–Kister (*9*), NRTL (*10*), and Van Laar extended by Van Ness (*11*). Coefficients of these equations were obtained by a modified Barker method (*12–14*). The molar second virial coefficients of the pure substances and of the mixtures were calculated according to Hayden and O'Connell (*15*). The molar liquid volumes were estimated according to Yen and Woods (*16*).

The picoline systems can be described by any equation with nearly the same accuracy. For pyridine-containing systems, the use of more flexible equations, e.g., the Redlich–Kister or Van Laar–Van Ness, can improve description.

Results of fitting all the binary data with the Wilson equation

$$G^E/RT = -x_1 \ln (x_1 + \Lambda_{12}x_2) - x_2 \ln (x_2 + \Lambda_{21}x_1) \quad (1)$$

the coefficients Λ_{12} and Λ_{21} together with their standard errors $\sigma(\Lambda_{ij})$ and the correlation coefficients q for pairs $(\Lambda_{12}, \Lambda_{21})$ are given in Table III.

Literature Cited

(1) Warycha, S. *Z. Phys. Chem. (Leipzig)* **1977**, *258*, 864.
(2) Warycha, S. *J. Chem. Thermodyn.* **1977**, *9*, 813.
(3) Warycha, S.; Rytting J. H. *J. Solution Chem.* **1984**, *13*, 589.
(4) Wawer, I.; Warycha, S. *Pol. J. Chem.* **1985**, *59*, 565.
(5) Herington, E. F. G.; Martin, J. F. *Trans. Faraday Soc.* **1953**, *49*, 154.
(6) Boublik, T.; Fried, V.; Hala, E. *The Vapour Pressures of Pure Substances*; Elsevier: Amsterdam, 1973.
(7) Janaszewski, B.; Oracz, P.; Góral, M.; Warycha, S. *Fluid Phase Equilib.* **1982**, *9*, 295.
(8) Wilson, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 127.
(9) Redlich, O.; Kister, A. T. *Ind. Eng. Chem.* **1948**, *40*, 345.
(10) Renon, H.; Prausnitz, J. M. *AIChE J.* **1968**, *14*, 135.
(11) Van Ness, H. C. *Classical Thermodynamics of Non-Electrolyte Solutions*; Pergamon: London, 1964.
(12) Góral, M. *Z. Phys. Chem. (Leipzig)* **1977**, *258*, 1040.
(13) Góral, M.; Janaszewski, B. *Z. Phys. Chem. (Leipzig)* **1977**, *258*, 417.
(14) Kolasińska, G.; Oracz, P. *Z. Phys. Chem. (Leipzig)* **1979**, *260*, 169.
(15) Hayden, J. G.; O'Connell, J. R. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209.
(16) Yen, L. C.; Woods, S. S. *AIChE J.* **1966**, *12*, 95.

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