Article

Vapor–Liquid Equilibrium Data for Binary Systems of 1H-Pyrrole with Butan-1-ol, Propan-1-ol, or Pentan-1-ol

Maciej Zawadzki,[†] Peterson Thokozani Ngema,[‡] Urszula Domanska,[†,‡] Paramespri Naidoo,[‡] and Deresh Ramjugernath*,[‡]

[†]Physical Chemistry Division, Faculty of Chemistry, Warsaw University of Technology, 00-664 Warsaw, Poland

[‡]Thermodynamics Research Unit, School of Engineering, University of KwaZulu-Natal, Howard College Campus, Durban, 4041, South Africa

ABSTRACT: Isobaric and isothermal vapor–liquid equilibrium (VLE) data are presented for binary systems comprising 1H-pyrrole (pyrolle) with light alcohols. The systems measured include 1H-pyrrole + butan-1-ol at 40 kPa and $T = (353.2, 363.2, \text{and } 373.2)$ K; 1H-pyrrole + propan-1-ol at 40 kPa and $T = (348.2, 358.2, \text{and } 368.2)$ K; and 1H-pyrrole + pentan-1-ol at 40 kPa and $T = (353.2, 363.2, \text{and } 373.2)$ K. Measurements were undertaken on a low-pressure dynamic still, with analysis of the equilibrium samples by gas chromatography. The 1H-pyrolle + butan-1-ol and 1H-pyrolle + pentan-1-ol systems exhibited azeotropic behavior for both the isobaric and the isothermal measurements. The measured data were modeled using the Wilson and nonrandom two-liquid (NRTL) excess Gibbs energy models, with both models correlating the data well.
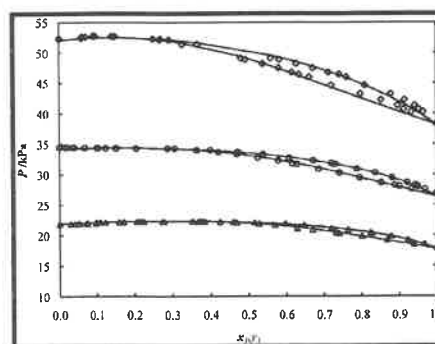
INTRODUCTION

Pyrrole is a heterocyclic aromatic organic compound which is a five-membered ring with the formula C_4H_4NH.[1] It is a colorless volatile liquid that darkens readily upon exposure to air. Substituted derivatives are also called pyrroles, for example, N-methylpyrrole, $C_4H_4NCH_3$. Porphobilinogen, a trisubstituted pyrrole is the biosynthetic precursor to many natural products such as heme.[2] Heme is a prosthetic group that consists of an iron atom contained in the center of a large heterocyclic organic ring. Pyrroles are components of more complex macrocycles, including the porphyrins of heme, chlorins, bacteriochlorins, chlorophyll, and porphyrinogens. Pyrrole has no significant commercial application, but N-methylpyrrole is a precursor to N-methylpyrrolecarboxylic acid, a building block in pharmaceutical chemistry.[3]

The aim of the present work is to study vapor–liquid equilibria so as to obtain insight into 1H-pyrrole alcohol mixtures. Thus, isothermal and isobaric measurements were undertaken for 1H-pyrolle + {butan-1-ol, propan-1-ol, or pentan-1-ol}. Isobaric measurements for all systems were undertaken at 40 kPa. The isothermal measurements for 1H-pyrrole + butan-1-ol were undertaken at $T = (353.2, 363.2, \text{and } 373.2)$ K; 1H-pyrrole + propan-1-ol at $T = (348.2, 358.2, \text{and } 368.2)$ K; and 1H-pyrrole + pentan-1-ol at $T = (353.2, 363.2, \text{and } 373.2)$ K.

The measured data will be modeled to calculate interaction parameters for 1H-pyrrole mixtures in terms of the dispersive quasichemical activity coefficient (DISQUAC) model.[4,5] Imidazoles contain two aromatic nitrogen groups, one similar to pyridine[6,7] and the other to 1H-pyrrole. Knowing interaction parameters for these groups will allow one to predict the properties of mixtures containing imidazoles that were previously

Table 1. Property Data for the Chemicals Studied

	butan-1-ol	propan-1-ol	pentan-1-ol	1H-pyrrole
	$n_D*,^a$			
measured	1.3993	1.3851	1.4097	1.5103
literature[17]	1.3988	1.3850	1.4101	1.5085
	$\rho*,^b/\text{kg}\cdot\text{m}^{-3}$			
measured	810.2	801.3	816.1	970.4
literature[17]	809.5	799.7	814.4	969.8
GC peak area (area fraction)	1.000	0.999	0.999	1.000
claimed purity (mass fraction)	≥ 0.999	≥ 0.998	≥ 0.994	≥ 0.990
Critical Properties[18]				
T_c/K	563.05	536.78	588.15	639.70
P_c/kPa	4423.00	5167.57	3909.00	6330.00
$V_c/\text{cm}^3\cdot\text{mol}^{-1}$	275.0	218.5	326.0	200.0
acentric factor (ω)	0.590	0.629	0.579	0.325
Antoine Constants[12,c,d]				
A	10.27539	10.12822	11.08152	9.30892
B	3294.10	3011.64	4281.65	2993.29
C	55.42	45.72	111.88	63.32

^{a}Refractive index at 293.2 K, uncertainty = ± 0.0018. ^{b}Density at 293.2 K, uncertainty = ± 0.0017 g·cm^{-3}. ^{c}Equation: $\log_{10}(P/\text{kPa}) = A - B/(T/\text{K} + C)$. ^{d}Constants from ref 12 parametrized for units of temperature in K and pressure in kPa.
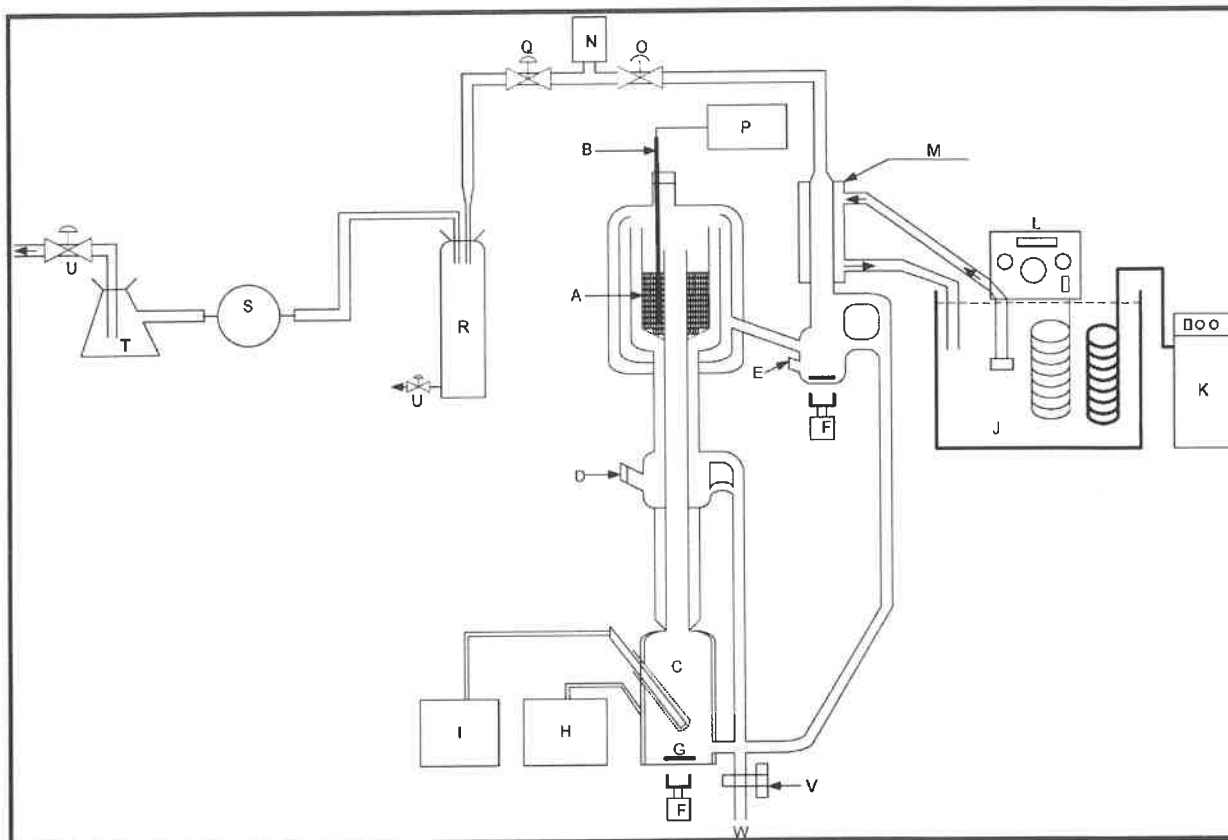
Figure 1. Schematic diagram for the low-pressure VLE still: A, packing chamber; B, Pt-100; C, reboiler; D, liquid sampling point; E, vapor sampling point; G, magnetic stirrer; H, external heater; I, internal heat; J, water bath with chilling fluid; K, cold finger; L, temperature programmable circulator; M, condenser; N, pressure transducer; O, control valve; P, digital multimeter; Q, fine tune valve; R, ballast; S, vacuum pump; T, vacuum flask; U, vent valve to atmosphere; V, drain valve and W, drain.

Table 2. Measured Vapor Pressure for the Chemicals Studied[a,b]

	1H-pyrrole		propan-1-ol		butan-1-ol		pentan-1-ol	
P/kPa	exp T/K	ΔT^c	exp T/K	ΔT^c	exp T/K	ΔT^c	exp T/K	ΔT^c
10	339.9	0.09	319.6	0.08	337.2	0.01	353.8	0.07
20	356.2	0.06	332.8	0.04	351.1	0.10	368.7	0.04
30	366.5	0.04	341.3	0.03	360.0	0.08	378.2	0.09
40	374.5	0.08	347.7	0.02	366.7	0.09	385.3	0.08
50	380.8	0.06	352.7	0.07	372.1	0.10	391.0	0.04
60	386.1	0.09	357.2	0.06	376.6	0.10	395.9	0.03
70	390.9	0.09	360.8	0.09	380.5	0.10	400.1	0.04
80	395.2	0.04	364.1	0.08	384.0	0.09	404.0	0.07
90	399.1	0.09	367.1	0.07	387.2	0.09	407.4	0.06
99.7	402.4	0.09	369.8	0.06	390.2[d]	0.01[d]	410.3	0.06

[a]$u(T)$ = 0.1 K. [b]$u(P)$ = 0.3 kPa. [c]Literature vapor pressure data obtained from DDB.[12] [d]Measured at 99.9 kPa.

$$\Delta T = |T_{lit} - T_{exp}|$$

measured in our laboratories. This will enable a test of the model consistency.

EXPERIMENTAL SECTION

Materials. The purities of the chemical used in the study are listed in Table 1. All chemicals (except butan-1-ol) were purchased from Capital Laboratories. Butan-1-ol was obtained from Merck. Gas chromatography (GC) analysis revealed no

significant impurities, and the measured refractive indices and densities agree closely with literature. The refractive indices were measured using an ATAGO RX-7000α refractometer with a reported uncertainty of ± 0.0018 in refractive index. The densities of the chemicals were measured using an Anton Paar DMA 5000 density meter with a reported uncertainty of ± 0.0017 g·cm⁻³.

Equipment. A vapor and liquid recirculating still as described by Joseph et al.[8] was used to measure the phase equilibrium data.

Table 3. P−x−y Data for the 1H-Pyrrole (1) + Propan-1-ol (2) System at (348.2, 358.2, and 368.2) K[a,b,c,d]

	T/K = 348.2					T/K = 358.2			
x_1	P/kPa	y_1	γ_1	γ_2	x_1	P/kPa	y_1	γ_1	γ_2
0.000	40.9	0.000		1.00	0.000	62.7	0.000		1.00
0.155	37.1	0.082	1.36	0.98	0.056	61.2	0.029	1.45	1.00
0.240	35.6	0.129	1.33	1.00	0.134	58.7	0.070	1.41	1.01
0.329	34.1	0.176	1.27	1.02	0.156	57.7	0.082	1.39	1.00
0.345	33.7	0.186	1.26	1.02	0.181	57.2	0.096	1.39	1.01
0.419	32.3	0.226	1.21	1.05	0.230	55.3	0.127	1.40	1.00
0.536	30.4	0.295	1.16	1.13	0.329	52.4	0.174	1.27	1.03
0.640	28.6	0.366	1.14	1.23	0.351	51.7	0.183	1.24	1.04
0.716	26.9	0.434	1.13	1.31	0.401	50.2	0.215	1.23	1.05
0.767	25.2	0.487	1.11	1.36	0.474	47.7	0.254	1.17	1.08
0.813	23.9	0.535	1.09	1.45	0.539	45.6	0.296	1.15	1.11
0.848	22.4	0.600	1.10	1.44	0.610	43.0	0.340	1.10	1.16
0.897	20.3	0.681	1.07	1.54	0.736	37.7	0.451	1.06	1.25
0.929	19.0	0.752	1.07	1.62	0.789	35.3	0.505	1.04	1.32
0.965	16.9	0.858	1.04	1.67	0.830	33.2	0.560	1.03	1.37
1.000	14.4	1.000	1.00		0.873	30.6	0.635	1.02	1.40
					0.908	28.5	0.704	1.02	1.46
					0.940	26.2	0.785	1.00	1.50
					0.968	24.3	0.871	1.00	1.56
					0.983	23.0	0.929	1.00	1.53
					0.989	22.5	0.956	1.00	1.43
					1.000	21.8	1.000	1.00	

		T/K = 368.2		
x_1	P/kPa	y_1	γ_1	γ_2
0.000	94.0	0.000		1.00
0.100	88.7	0.050	1.38	1.00
0.200	85.0	0.099	1.31	1.02
0.265	82.6	0.141	1.37	1.03
0.338	78.7	0.180	1.31	1.04
0.405	74.4	0.221	1.27	1.04
0.535	69.4	0.297	1.20	1.12
0.640	64.1	0.360	1.13	1.21
0.765	56.5	0.472	1.09	1.35
0.798	53.2	0.517	1.07	1.35
0.869	47.7	0.615	1.05	1.49
0.919	42.1	0.723	1.03	1.53
0.939	39.6	0.778	1.02	1.53
0.989	32.9	0.934	0.97	2.10
1.000	32.1	1.000	1.00	

$^a u(T) = 0.1$ K. $^b u(P) = 0.3$ kPa. $^c u(x_1) = 0.006$. $^d u(y_1) = 0.006$.

Table 4. P−x−y Data for the 1H-Pyrrole (1) + Butan-1-ol (2) System at (353.2, 363.2, and 373.2) K[a,b,c,d]

	T/K = 353.2					T/K = 363.2			
x_1	P/kPa	y_1	γ_1	γ_2	x_1	P/kPa	y_1	γ_1	γ_2
0.000	21.8	0.000		1.00	0.000	34.5	0.000		1.00
0.029	21.9	0.041	1.72	0.99	0.015	34.5	0.021	1.79	0.99
0.052	22.0	0.075	1.76	0.98	0.037	34.5	0.040	1.39	1.00
0.071	22.0	0.097	1.67	0.98	0.067	34.4	0.068	1.30	1.00
0.098	22.1	0.108	1.35	1.00	0.100	34.4	0.104	1.33	0.99
0.110	22.1	0.123	1.37	1.00	0.124	34.3	0.125	1.29	0.99
0.159	22.2	0.171	1.33	1.00	0.153	34.3	0.151	1.26	1.00
0.207	22.3	0.215	1.28	1.01	0.204	34.3	0.204	1.28	0.99
0.213	22.3	0.223	1.30	1.01	0.306	34.3	0.288	1.20	1.02
0.274	22.3	0.278	1.26	1.02	0.399	34.0	0.364	1.15	1.04
0.376	22.3	0.352	1.16	1.06	0.472	33.7	0.420	1.11	1.07
0.383	22.3	0.368	1.19	1.05	0.538	33.3	0.470	1.08	1.11
0.460	22.2	0.424	1.14	1.08	0.607	32.8	0.525	1.05	1.15
0.516	22.1	0.469	1.11	1.11	0.672	32.2	0.578	1.03	1.20
0.597	21.9	0.528	1.08	1.17	0.719	31.8	0.616	1.01	1.26
0.648	21.7	0.569	1.06	1.22	0.729	31.6	0.629	1.01	1.26
0.719	21.1	0.629	1.03	1.28	0.787	30.9	0.686	1.00	1.32
0.763	20.9	0.670	1.02	1.33	0.836	30.3	0.740	1.00	1.39
0.823	20.4	0.731	1.01	1.42	0.880	29.4	0.795	0.99	1.46
0.827	20.3	0.739	1.01	1.40	0.921	28.6	0.852	0.99	1.55
0.879	19.9	0.801	1.00	1.50	0.943	28.2	0.889	0.99	1.59
0.923	19.2	0.867	1.00	1.52	0.950	28.0	0.900	0.99	1.62
0.968	18.5	0.939	1.00	1.62	0.969	27.6	0.933	0.99	1.73
1.000	18.0	1.000	1.00		1.000	26.9	1.000	1.00	

		T/K = 373.2		
x_1	P/kPa	y_1	γ_1	γ_2
0.000	52.3	0.000		1.00
0.059	52.5	0.060	1.40	1.00
0.071	52.6	0.061	1.18	1.02
0.096	52.7	0.091	1.31	1.01
0.150	52.7	0.141	1.30	1.02
0.269	52.3	0.250	1.27	1.03
0.292	52.1	0.267	1.25	1.03
0.366	51.4	0.326	1.20	1.04
0.559	49.1	0.481	1.10	1.10
0.582	48.9	0.493	1.08	1.13
0.628	48.2	0.538	1.08	1.14
0.672	47.5	0.580	1.07	1.16
0.712	46.8	0.616	1.06	1.19
0.740	46.4	0.635	1.04	1.25
0.759	46.0	0.662	1.05	1.23
0.809	44.7	0.719	1.04	1.26
0.878	43.2	0.797	1.03	1.37
0.914	42.2	0.852	1.03	1.39
0.942	41.3	0.896	1.03	1.42
0.953	40.7	0.912	1.02	1.46
0.965	40.3	0.933	1.02	1.47
1.000	38.2	1.000	1.00	

$^a u(T) = 0.1$ K. $^b u(P) = 0.3$ kPa. $^c u(x_1) = 0.006$. $^d u(y_1) = 0.006$.

The still features a central vacuum-jacketed Cottrell pump and a packed equilibrium chamber (see Figure 1). The disengaged vapor and liquid phases are sampled through septa. Vapor–liquid equilibrium (VLE) measurements for mixtures of various compositions can, therefore, be made without interruption of the boiling. To improve mixing and to promote smooth boiling, the boiling chamber and condensate receiver were magnetically stirred.

The pressure in the VLE still was controlled with a KNF vacuum pump controller (type NC800). A Sensotec Super TJE pressure transducer was used for the measurement of the pressure. The pressure transducer was calibrated with a WIKA CPH 600 pressure transducer standard. The uncertainty in the reported pressure is ± 0.3 kPa.

The equilibrium temperature was measured in the packed equilibrium chamber by means of a Pt-100 sensor located near the bottom of the packed section. The temperature sensor was calibrated using a WIKA CTB 9100 (multimeter display CTH6500). The uncertainty in the reported temperature is estimated to be within ± 0.1 K. Isothermal operation was achieved by manually adjusting the pressure; that is, the pressure set-point was adjusted manually until each mixture reached the desired equilibrium temperature.

The contents of the still were assumed to be at equilibrium when the temperature remained constant (within experimental uncertainty) for at least 45 min. Once equilibrium was assumed, vapor and liquid samples were withdrawn for composition

Table 5. $P-x-y$ Data for the 1H-Pyrrole (1) + Pentan-1-ol (2) System at (353.2, 363.2, and 373.2) K[a,b,c,d]

	T/K = 353.2					T/K = 363.2			
x_1	P/kPa	y_1	γ_1	γ_2	x_1	P/kPa	y_1	γ_1	γ_2
0.000	9.8	0.000		1.00	0.000	15.6	0.000		1.00
0.063	10.7	0.142	1.34	1.00	0.028	16.2	0.060	1.29	1.00
0.108	11.6	0.219	1.30	1.03	0.066	16.9	0.131	1.25	1.01
0.119	11.8	0.243	1.34	1.03	0.140	18.4	0.244	1.19	1.04
0.157	12.3	0.305	1.33	1.03	0.226	19.9	0.374	1.22	1.03
0.212	13.1	0.390	1.34	1.03	0.227	19.9	0.383	1.25	1.02
0.294	14.1	0.482	1.28	1.05	0.312	21.1	0.467	1.18	1.05
0.368	14.8	0.543	1.21	1.09	0.329	21.7	0.497	1.22	1.04
0.441	15.5	0.605	1.18	1.11	0.390	22.6	0.554	1.19	1.06
0.506	16.0	0.654	1.15	1.14	0.465	23.5	0.612	1.15	1.10
0.555	16.3	0.685	1.12	1.17	0.522	24.3	0.655	1.13	1.12
0.612	16.6	0.720	1.09	1.22	0.581	24.9	0.693	1.10	1.17
0.662	16.8	0.749	1.05	1.27	0.632	25.4	0.726	1.09	1.21
0.721	17.0	0.778	1.02	1.38	0.683	25.7	0.759	1.06	1.25
0.824	17.5	0.855	1.01	1.47	0.733	26.0	0.790	1.04	1.31
0.897	17.6	0.909	0.99	1.59	0.763	26.1	0.807	1.03	1.37
0.902	17.7	0.916	1.00	1.55	0.902	26.5	0.905	0.99	1.65
1.000	18.0	1.000	1.00		1.000	26.9	1.000	1.00	

	T/K = 373.2			
x_1	P/kPa	y_1	γ_1	γ_2
0.000	24.3	0.000		1.00
0.009	24.5	0.018	1.28	1.00
0.052	26.4	0.093	1.24	1.04
0.114	28.0	0.198	1.27	1.05
0.147	29.0	0.240	1.24	1.07
0.190	30.2	0.308	1.28	1.06
0.216	30.9	0.332	1.24	1.08
0.253	31.8	0.394	1.30	1.06
0.322	33.2	0.450	1.21	1.11
0.381	34.2	0.505	1.19	1.13
0.409	34.7	0.545	1.21	1.10
0.473	35.5	0.593	1.16	1.13
0.562	36.6	0.669	1.14	1.14
0.618	37.0	0.693	1.08	1.23
0.731	37.8	0.777	1.05	1.29
0.798	38.2	0.817	1.02	1.43
0.850	38.6	0.869	1.03	1.39
0.878	38.6	0.892	1.03	1.41
0.938	38.6	0.941	1.01	1.52
0.977	38.4	0.977	1.00	1.58
0.991	38.3	0.982	0.99	3.16
1.000	38.2	1.000	1.00	

[a]$u(T)$ = 0.1 K. [b]$u(P)$ = 0.3 kPa. [c]$u(x_1)$ = 0.006. [d]$u(y_1)$ = 0.006.

analysis. The equilibrium phases were analyzed using a Shimadzu GC-2010 GC equipped with a thermal conductivity detector (TCD). The GC column used was a Cwax 20 M Bonded column which provided excellent separation of the components. The procedure used for calibrating the GC detector was the area ratio method, as discussed by Raal and Mühlbauer.[9] The estimated uncertainty in the phase compositions is ± 0.006 mole fraction.

■ CORRELATIONS

The $\gamma-\phi$ method was used to regress the experimental VLE data using eq 1 below,

$$y_i \Phi_i P = x_i \gamma_i P_i^{\mathrm{sat}} \qquad (1)$$

where y_i is the vapor phase mole fraction of species i, x_i is the liquid phase mole fraction of species i, γ_i is the activity coefficient

Table 6. Regressed Model Parameters for the 1H-Pyrrole + Propan-1-ol, Butan-1-ol, and Pentan-1-ol Systems

1H-pyrrole (1) + propan-1-ol (2)			
	T/K = 348.2	T/K = 358.2	T/K = 368.2
NRTL			
$(g_{12} - g_{11})$/J·mol⁻¹	3811.4	1874.0	1071.8
$(g_{21} - g_{22})$/J·mol⁻¹	−1137.9	−290.3	747.9
ΔP^a/kPa	0.28	0.09	0.57
Δy_2^a	0.014	0.005	0.012
Wilson			
$(\lambda_{12} - \lambda_{11})$/J·mol⁻¹	−667.9	72.6	198.5
$(\lambda_{21} - \lambda_{22})$/J·mol⁻¹	3371.2	1499.8	1798.9
ΔP^a/kPa	0.33	0.09	0.39
Δy_2^a	0.014	0.006	0.011

1H-pyrrole (1) + butan-1-ol (2)			
	T/K = 353.2	T/K = 363.2	T/K = 373.2
NRTL			
$(g_{12} - g_{11})$/J·mol⁻¹	3189.8	2709.5	736.7
$(g_{21} - g_{22})$/J·mol⁻¹	−1099.2	−916.8	677.2
ΔP^a/kPa	0.05	0.07	0.29
Δy_2^a	0.007	0.004	0.007
Wilson			
$(\lambda_{12} - \lambda_{11})$/J·mol⁻¹	−49.3	61.4	1556.3
$(\lambda_{21} - \lambda_{22})$/J·mol⁻¹	2142.1	1801.4	−125.0
ΔP^a/kPa	0.05	0.06	0.29
Δy_2^a	0.007	0.004	0.007

1H-pyrrole (1) + pentan-1-ol (2)			
	T/K = 353.2	T/K = 363.2	T/K = 373.2
NRTL			
$(g_{12} - g_{11})$/J·mol⁻¹	1903.9	3931.1	1713.5
$(g_{21} - g_{22})$/J·mol⁻¹	42.9	−1372.5	143.8
ΔP^a/kPa	0.06	0.06	0.09
Δy_2^a	0.012	0.010	0.014
Wilson			
$(\lambda_{12} - \lambda_{11})$/J·mol⁻¹	1482.7	161.7	1644.8
$(\lambda_{21} - \lambda_{22})$/J·mol⁻¹	485.1	2547.8	235.3
ΔP^a/kPa	0.06	0.07	0.09
Δy_2^a	0.012	0.010	0.014

[a]Calculated using eq 5.
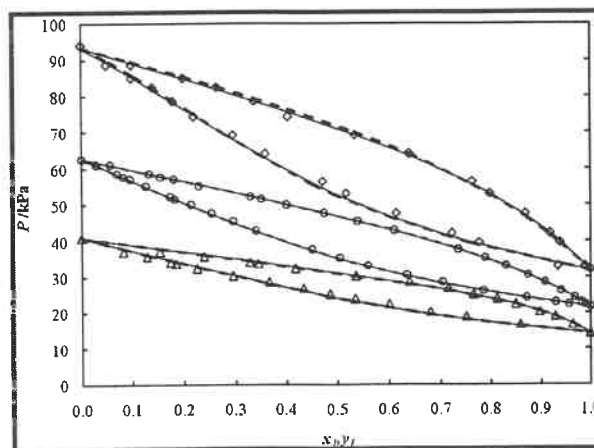
Figure 2. $P-x-y$ data for the 1H-pyrrole (1) + propan-1-ol (2) system. Experimental: △, 348.2 K; ○, 358.2 K; ◊, 368.2 K; ——, Wilson model; ----, NRTL model.
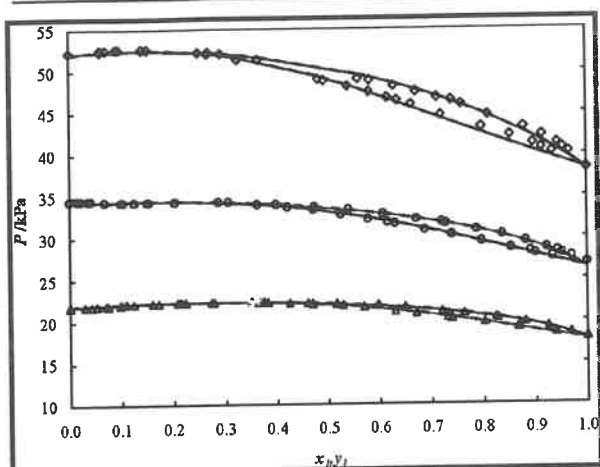
Figure 3. P–x–y data for the 1H-pyrrole (1) + butan-1-ol (2) system. Experimental: △, 353.2 K; ○, 363.2 K; ◇, 373.2 K; ——, Wilson model; ----, NRTL model.

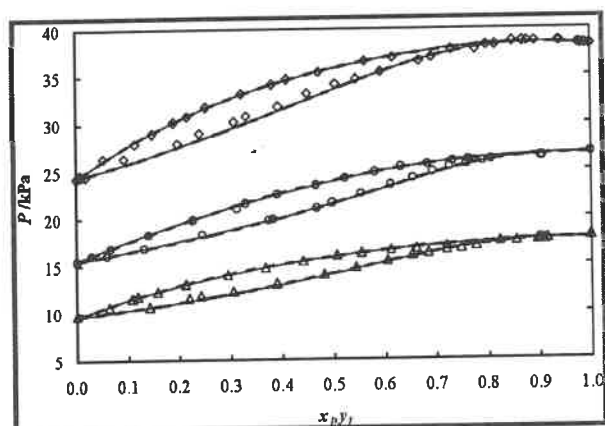**Figure 4.** P–x–y data for the 1H-pyrrole (1) + pentan-1-ol (2) system. Experimental: △, 353.2 K; ○, 363.2 K; ◇, 373.2 K; ——, Wilson model; ----, NRTL model.

Table 7. Correlation Analysis for the 1H-Pyrrole + Propan-1-ol, Butan-1-ol (2), and Pentan-1-ol (2) Systems

	NRTL		Wilson	
	y_2	P/kPa	y_2	P/kPa
1H-Pyrrole (1) + Propan-1-ol (2)				
T/K = 348.2				
BIAS%[a]	0.947	−0.08	1.041	−0.22
AAD%[b]	0.798	0.96	0.621	1.10
T/K = 358.2				
BIAS%[a]	1.066	−0.09	1.189	−0.08
AAD%[b]	0.955	0.26	0.869	0.26
T/K = 368.2				
BIAS%[a]	−0.072	0.01	0.024	0.09
AAD%[b]	0.596	0.94	0.229	0.67
1H-Pyrrole (1) + Butan-1-ol (2)				
T/K = 353.2				
BIAS%[a]	−0.287	0.01	−0.233	0.04
AAD%[b]	0.961	0.23	1.096	0.24
T/K = 363.2				
BIAS%[a]	1.161	0.16	1.074	0.12
AAD%[b]	0.273	0.24	0.205	0.22
T/K = 373.2				
BIAS%[a]	−0.331	0.11	−0.331	0.01
AAD%[b]	0.332	0.17	0.332	0.17
1H-Pyrrole (1) + Pentan-1-ol (2)				
T/K = 353.2				
BIAS%[a]	−0.399	0.07	−0.388	0.09
AAD%[b]	0.408	0.45	0.406	0.45
T/K = 363.2				
BIAS%[a]	−0.278	−0.07	−0.282	−0.05
AAD%[b]	0.273	0.23	0.281	0.29
T/K = 373.2				
BIAS%[a]	−0.343	−0.01	−0.493	−0.02
AAD%[b]	0.734	0.29	0.851	0.29

[a]Calculated using eq 3. [b]Calculated using eq 4.

$$BIAS(U) = \frac{100}{N} \cdot \sum \left(\frac{U_{exp} - U_{cal}}{U_{exp}} \right) \tag{3}$$

$$AAD(U) = \frac{100}{N} \cdot \sum \left| \frac{U_{exp} - U_{cal}}{U_{exp}} \right| \tag{4}$$

$$\Delta U = \frac{1}{N} \cdot \sum |U_{cal} - U_{exp}| \tag{5}$$

of species i, Φ_i is the vapor correction factor which is the ratio of the fugacity coefficient to the saturated fugacity coefficient multiplied by the Poynting correction factor, P is the total pressure, and P_i^{sat} is the saturation pressure of species i. If the vapor phase is assumed to be ideal ($\Phi_i = 1$), then eq 1 reduces to modified Raoult's law.

The NRTL[10] and the Wilson[11] excess Gibbs models were used in conjunction with bubble-pressure and bubble-temperature calculation algorithms to regress for the model parameters. The data reduction procedure requires minimization of an objective function (OF). For the isothermal and isobaric data the objective function given in eq 2 was used, where δS, the pressure residual, or temperature residual is the difference between the measured and the calculated pressures or temperatures:

$$OF = \sum |\delta S| \tag{2}$$

where S represents P or T. Equations 3, 4, and 5 represent the BIAS, the average absolute deviations (AAD), and absolute deviations, respectively, where U represents P, T, or y.

■ RESULTS AND DISCUSSION

Table 1 lists the critical properties and the acentric factors for the chemicals used in this study. Pure component vapor pressure data were measured for all chemicals used in this investigation. Table 2 lists the measured and calculated vapor pressures (from Antoine constants[12]). The Antoine constants used from literature are presented in Table 1 as well.

VLE measurements were performed for the systems 1H-pyrrole + butan-1-ol at 40 kPa and T = (353.2, 363.2, and 373.2) K; 1H-pyrrole + propan-1-ol at 40 kPa and T = (348.2, 358.2, and 368.2) K; and 1H-pyrrole + pentan-1-ol at 40 kPa and T = (353.2, 363.2, and 373.2) K. The experimental isothermal data are listed in Tables 3 to 5 with the regressed model parameters presented in Table 6. The isothermal data are shown graphically in Figures 2 to 4. The NRTL nonrandom (α_{ij})
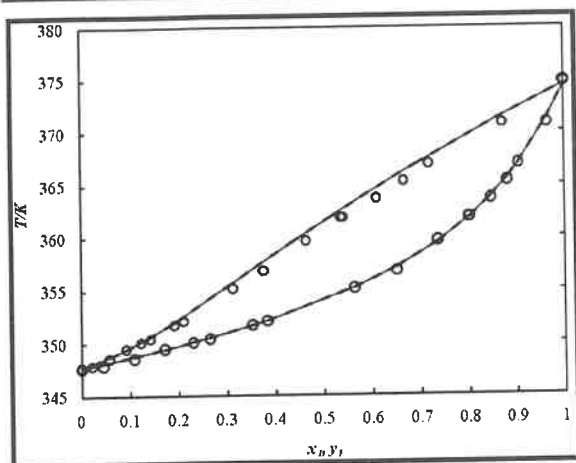
Figure 5. $T-x-y$ data for the 1H-pyrrole (1) + propan-1-ol (2) system at 40 kPa. O, experimental; ——, Wilson model; ----, NRTL model.

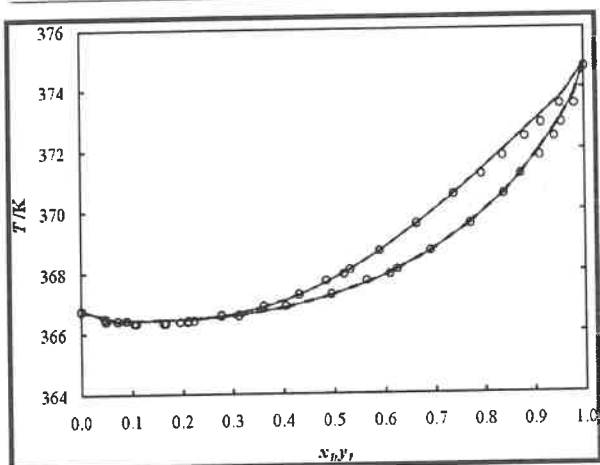Figure 6. $T-x-y$ data for the 1H-pyrrole (1) + butan-1-ol (2) system at 40 kPa. O, experimental; ——, Wilson model; ----, NRTL model.
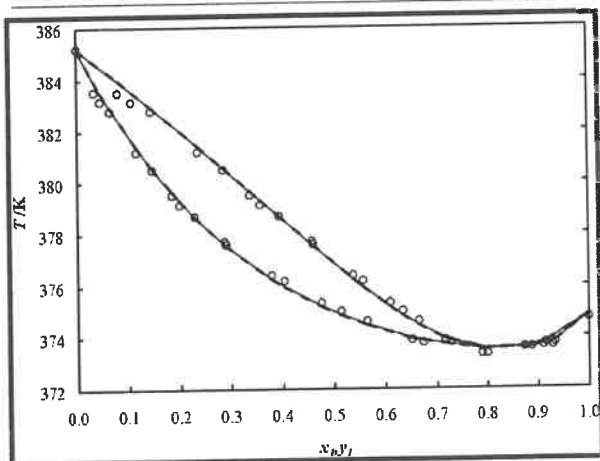

Figure 7. $T-x-y$ data for the 1H-pyrrole (1) + pentan-1-ol (2) system at 40 kPa. O, experimental; ——, Wilson model; ----, NRTL model.

parameter in the NRTL model was set to 0.4 as suggested in literature[13] for systems containing alcohols. With respect to the isothermal measurements, the 1H-pyrrole + propan-1-ol system

Table 8. $T-x-y$ Data for the 1H-Pyrrole + {Propan-1-ol/Butan-1-ol/Pentan-1-ol} Systems at 40 kPa[a,b,c,d]

x_1	T/K	y_1	γ_1	γ_2	x_1	T/K	y_1	γ_1	γ_2
1H-Pyrrole (1) + Propan-1-ol (2)					1H-Pyrrole (1) + Butan-1-ol (2)				
0.000	347.6	0.000		1.00	0.000	366.8	0.000		1.00
0.045	347.9	0.023	1.43	1.01	0.048	366.5	0.047	1.31	1.01
0.108	348.5	0.058	1.47	1.02	0.049	366.4	0.049	1.34	1.02
0.171	349.4	0.091	1.40	1.01	0.072	366.4	0.071	1.32	1.02
0.230	350.1	0.122	1.36	1.02	0.090	366.4	0.089	1.33	1.02
0.265	350.4	0.142	1.35	1.03	0.105	366.3	0.109	1.40	1.02
0.354	351.7	0.191	1.29	1.05	0.168	366.4	0.164	1.31	1.02
0.385	352.1	0.211	1.29	1.06	0.210	366.4	0.195	1.25	1.04
0.565	355.1	0.314	1.16	1.14	0.223	366.4	0.211	1.27	1.03
0.652	356.8	0.378	1.13	1.21	0.312	366.6	0.278	1.19	1.06
0.736	359.6	0.463	1.09	1.22	0.405	366.9	0.362	1.18	1.07
0.801	361.9	0.537	1.07	1.27	0.495	367.3	0.431	1.13	1.10
0.802	361.9	0.541	1.07	1.27	0.564	367.7	0.485	1.10	1.14
0.846	363.6	0.609	1.07	1.30	0.610	367.9	0.520	1.08	1.17
0.882	365.3	0.665	1.05	1.36	0.625	368.1	0.532	1.07	1.18
0.904	366.9	0.718	1.05	1.32	0.690	368.7	0.589	1.05	1.22
0.964	370.8	0.872	1.03	1.38	0.771	369.6	0.663	1.02	1.31
1.000	374.7	1.000	1.00		0.838	370.5	0.737	1.01	1.39
					0.873	371.2	0.794	1.02	1.35
					0.912	371.8	0.837	1.01	1.50
					0.941	372.4	0.882	1.01	1.58
					0.954	372.9	0.914	1.01	1.45
					0.980	373.4	0.952	1.01	1.83
					1.000	374.7	1.000	1.00	
1H-Pyrrole (1) + Pentan-1-ol (2)									
0.000	385.2	0.000		1.00					
0.034	383.6	0.080	1.71	1.02					
0.046	383.2	0.107	1.72	1.01					
0.064	382.8	0.144	1.68	1.01					
0.115	381.2	0.236	1.62	1.01					
0.147	380.5	0.286	1.57	1.01					
0.184	379.5	0.338	1.54	1.02					
0.199	379.2	0.357	1.52	1.02					
0.229	378.7	0.394	1.48	1.02					
0.289	377.7	0.458	1.41	1.03					
0.291	377.6	0.459	1.41	1.04					
0.379	376.4	0.538	1.32	1.07					
0.404	376.2	0.557	1.30	1.07					
0.476	375.3	0.609	1.24	1.12					
0.514	375.1	0.633	1.20	1.14					
0.563	374.6	0.664	1.17	1.19					
0.651	373.9	0.716	1.12	1.30					
0.673	373.8	0.729	1.11	1.33					
0.789	373.3	0.800	1.06	1.55					
0.888	373.6	0.874	1.01	1.81					
0.928	373.6	0.911	1.01	1.99					
0.933	373.8	0.916	1.00	2.00					
1.000	374.7	1.000	1.00						

$^a u(T) = 0.1$ K. $^b u(P) = 0.3$ kPa. $^c u(x_1) = 0.006.$ $^d u(y_1) = 0.006.$

does not exhibit azeotropic behavior, while the 1H-pyrrole + {butan-1-ol/pentan-1-ol} systems each exhibited a maximum pressure azeotrope. Table 10 reveals that the azeotrope compositions (in terms of pyrolle mole fraction) decrease as the equilibrium pressure and temperature increases. The behavior seen is consistent with Wrewki's law[14] which states that the positive azeotrope becomes impoverished in the component characterized by the lowest heat of vaporization as pressure and temperature

Table 9. Regressed Model Parameters and Correlation Analysis for the 1H-Pyrrole (1) + {Propan-1-ol/Butan-1-ol/Pentan-1-ol} (2) Systems at 40 kPa

	1H-pyrrole + propan-1-ol	1H-pyrrole + butan-1-ol	1H-pyrrole + pentan-1-ol
NRTL			
$(g_{12} - g_{11})$/J·mol^{-1}	585.0	1230.6	2211.5
$(g_{21} - g_{22})$/J·mol^{-1}	900.7	224.5	180.3
ΔT^a/K	0.13	0.08	0.14
$\Delta y_1{}^a$	0.014	0.004	0.002
BIAS%^{b} (y_2)	1.369	−0.808	−0.011
AAD%^{c} (y_2)	0.188	0.124	0.899
BIAS%^{b} (T/K)	−0.02	−0.02	−0.01
AAD%^{c} (T/K)	0.04	0.02	0.04
Wilson			
$(\lambda_{12} - \lambda_{11})$/J·mol^{-1}	1070.4	1165.8	1440.2
$(\lambda_{21} - \lambda_{22})$/J·mol^{-1}	433.8	302.2	1181.9
ΔT^a/K	0.13	0.08	0.14
$\Delta y_1{}^a$	0.014	0.004	0.001
BIAS%^{b} (y_2)	1.061	−0.808	−0.011
AAD%^{c} (y_2)	0.215	0.183	0.997
BIAS%^{b} (T/K)	−0.02	−0.01	−0.01
AAD%^{c} (T/K)	0.04	0.02	0.03

^{a}Calculated using eq 5. ^{b}Calculated using eq 3. ^{c}Calculated using eq 4.

Table 10. Computed Azeotropic Conditions for the Systems Measured

system	composition (x_1)	T/K	P/kPa
1H-pyrrole (1) + butan-1-ol (2)	0.038	366.4	40.0
1H-pyrrole (1) + butan-1-ol (2)	0.264	353.2	22.3
1H-pyrrole (1) + butan-1-ol (2)	0.149	363.2	34.5
1H-pyrrole (1) + butan-1-ol (2)	0.004	373.2	52.5
1H-pyrrole (1) + pentan-1-ol (2)	0.821	373.6	40.0
1H-pyrrole (1) + pentan-1-ol (2)	0.995	353.2	17.6
1H-pyrrole (1) + pentan-1-ol (2)	0.914	363.2	26.5
1H-pyrrole (1) + pentan-1-ol (2)	0.950	373.2	38.4

increases. The BIAS and average absolute deviations (AADs) for the calculated pressure and vapor compositions of the NRTL and Wilson models are shown in Table 7. The Wilson model provides the best correlation of the isothermal data.

The isobaric data for the 1H-pyrrole + {propan-1-ol/butan-1-ol/pentan-1-ol} systems are shown in Figures 5 to 7. The isobaric data were also correlated using the NRTL and Wilson models; both models correlated the data well. The liquid molar volumes used in Wilson model were determined from the Rackett equation. The experimental data are listed in Table 8 with the regressed model parameters and correlation analysis given in Table 9. The 1H-pyrrole + {butan-1-ol/pentan-1-ol} systems each exhibited a minimum boiling azeotrope.

The point-to-point test[15] was employed to test the thermodynamic consistency of the experimental data measured in this study. The test specifies that data satisfies the test if the Δy values are less than 0.01. These values are listed in Tables 6 and 9 for the isothermal and isobaric data, respectively. The thermodynamics test is not a conclusive one as it is model-dependent, and therefore one can see that, depending on the model fitted to the data, the data either satisfies the test or marginally does not comply.

Table 10 lists the azeotropic points for the systems measured which exhibit azeotropic behavior. These points were computed using a polynomial fit of the x−y fit data and the temperature or pressure value was calculated using the intersection of all P−x and P−y curves or all T−x and P−y curves.

CONCLUSIONS

New isobaric and isothermal binary VLE data are presented for 1H-pyrrole + {propan-1-ol/butan-1-ol/pentan-1-ol}. Isobaric measurements were undertaken at 40 kPa, and isothermal data for 1H-pyrrole + butan-1-ol were measured at T = (353.2, 363.2, and 373.2) K; 1H-pyrrole + propan-1-ol at T = (348.2, 358.2, and 368.2) K; and 1H-pyrrole + pentan-1-ol at T = (353.2, 363.2, and 373.2) K. The 1H-pyrolle + butan-1-ol and 1H-pyrolle + pentan-1-ol systems exhibited azeotropic behavior for both the isobaric and isothermal measurements, while the 1H-pyrolle + propan-1-ol system did not exhibit azeotropic behavior. The experimental VLE data were successfully correlated using both the Wilson and the NRTL activity coefficients models.

AUTHOR INFORMATION

Corresponding Author

*E-mail: ramjuger@ukzn.ac.za. Tel.: +27 31 260 3128. Fax: +27 31 260 1118.

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