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Isobaric Vapor−Liquid Equilibria of the Ternary System Pentan-1-ol + Pentyl Acetate + Nonane

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ABSTRACT: Isobaric vapor−liquid equilibria (VLE) were measured for the ternary system pentan-1-ol + pentyl acetate + nonane and for one constituent binary system, pentan-1-ol + pentyl acetate, at the pressures (26.66, 53.33, 79.99, and 101.32) kPa. Boiling temperature (T)−liquid composition (x) relations were obtained by using a semimicroebulliometer. The Wilson equation was used to correlate the binary $T-x$ data and to predict VLE in the ternary system.

INTRODUCTION

The thermodynamic information of multicomponent vapor−liquid equilibria (VLE) is important for testing existing models, for promoting a general understanding of interactions in solutions, and in the design of equipment for separation processes.

In our previous papers[1−5] we presented experimental results of isobaric vapor−liquid equilibrium (VLE) for ternary systems, where the basic binary mixture was alkane (nonane)−alcohol (cyclohexanol, pentan-1-ol). Alkane−alcohol mixtures are used as suitable mixed solvents in the industry and laboratories. The third component was 1,2-dimethylbenzene,[1] hexan-2-one,[2,3] 1-butoxybutane,[4] and methoxybenzene.[5] We have used pentyl acetate as a good solvent for pigments and lacquers in the ternary systems 1,2-dimethylbenzene + pentyl acetate + nonane[6] and methylbenzene + ethylbenzene + pentyl acetate.[7]

In the present work, isobaric VLE data have been obtained at pressures (26.66, 53.33, 79.99, and 101.32) kPa for the ternary system pentan-1-ol + pentyl acetate + nonane, and for one constituent binary system, pentan-1-ol + pentyl acetate. No data for VLE of the ternary system have been found in the literature. VLE of the binary pentan-1-ol + pentyl acetate were studied by Lewell and Kristmanson[8] and Holley[9] at pressures of (100.765 and 102.658 kPa) correspondingly. The binary systems pentyl acetate + nonane and pentan-1-ol + nonane were studied in our papers.[3,4,6]

EXPERIMENTAL SECTION

Materials. Pentan-1-ol, pentyl acetate, and nonane used for the present measurements were the same as in our earlier works.[1,3,6] All substances were twice fractionally distilled in a high-efficiency Teflon rotor column. The samples were collected and stored under argon in glass ampules. The purity, checked by gas chromatography, was greater than 0.997. Densities, measured with a capillary pycnometer, and refractive indices, measured with a calibrated Abbe refractometer, thermostatted within 0.05 K, are compared in Table 1 with those reported in the literature together with normal boiling temperatures.

Table 1. Densities, ρ, Refractive Indices, n_D, at 293.13 K, and Normal Boiling Temperatures, T_b, of Pure Components

	ρ/kg·m^{-3}		n_D		T_b/K	
component	expt	lit.	expt	lit.	expt	lit.
pentan-1-ol	814.5	814.8[a]	1.4098	1.4100[a]	410.86	410.95[a]
pentyl acetate	875.4	875.3[a]	1.4027	1.4028[a]	422.59	422.35[a]
nonane	717.6	717.72[b]	1.4055	1.4054[b]	423.97	423.95[a]

[a] Ref 10. [b] Ref 11.

Table 2. Isobaric Vapor−Liquid Equilibrium Data: Liquid Phase, Mole Fraction (x_1), and Boiling Temperatures (T) in the Binary System Pentan-1-ol (1) + Pentyl Acetate (2)

	T/K at P/kPa			
x_1	P = 26.66	P = 53.33	P = 79.99	P = 101.32
0.000	380.05	400.72	414.20	422.59
0.100	378.25	398.62	411.91	420.18
0.200	376.97	397.00	410.07	418.16
0.306	375.70	395.31	408.08	415.97
0.391	375.08	394.41	406.98	414.80
0.485	374.59	393.74	406.09	413.44
0.593	374.40	393.00	405.12	412.60
0.697	374.31	392.61	404.48	411.87
0.785	374.38	392.44	404.14	411.37
0.871	374.78	392.49	403.98	411.10
0.928	375.09	392.58	403.96	410.98
1.000	375.63	392.70	403.80	410.86

Apparatus and Procedure. The boiling temperature−liquid composition ($T-x$) results were obtained at constant pressure in a semimicroebulliometer. The detailed description of the apparatus and procedure has been reported previously.[6,12] The boiling temperature of the liquid was measured by a specially manufactured thermistor. The pressures were determined using a well-type mercury manometer. The liquid mixtures were prepared by

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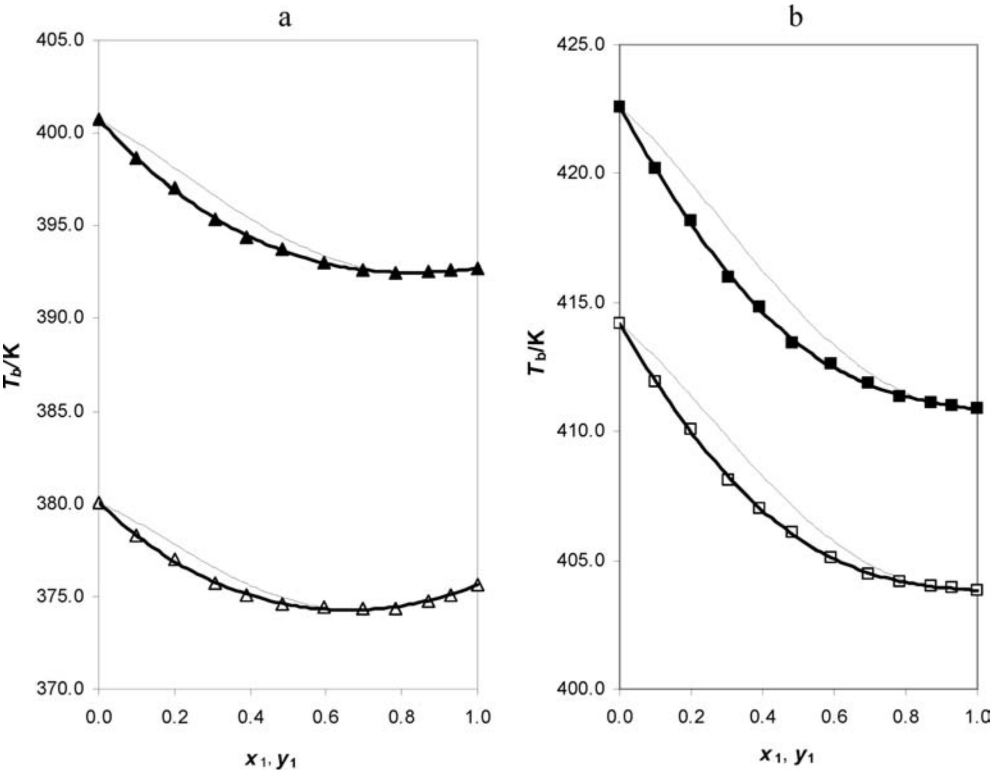

Figure 1. Experimental boiling temperature, T_b-x_1, diagrams for pentan-1-ol (1) + pentyl acetate (2) at pressures: (a) △, 26.66 kPa; ▲, 53.33 kPa; (b) □, 79.99 kPa; ■, 101.32 kPa. Calculated by the Wilson equation[13] curves: T_b-x_1 (bold lines), T_b-y_1 (thin lines).

Table 3. Values of $(\lambda_{ij} - \lambda_{ii})/R$ (the Wilson Equation[13]), Standard Deviations (σP; eq 2), and Mean Relative Differences (δP; eq 3) of Calculated Pressure for the Binary System Pentan-1-ol (1)−Pentyl Acetate (2)

	P/kPa = 26.66	P/kPa = 53.33	P/kPa = 79.99	P/kPa = 101.32
$(\lambda_{12} - \lambda_{11})/R/\text{J}\cdot\text{mol}^{-1}$	845.2	616.1	291.7	71.5
$(\lambda_{21} - \lambda_{22})/R/\text{J}\cdot\text{mol}^{-1}$	887.1	759.0	1046.8	1363.5
σP/kPa	0.095	0.192	0.288	0.413
100 δP	0.249	0.263	0.265	0.280

Table 4. Coefficients for the Antoine Vapor−Pressure Equation (eq 4)

component	A_i	B_i	C_i	temperature region/K
pentan-1-ol[a]	13.2675	2277.432	−147.537	375 to 415
pentyl acetate[b]	14.018	3215.228	−80.532	380 to 422
nonane[a]	13.8546	3224.816	−74.824	375 to 425

[a] Ref 4. [b] Ref 6.

Table 5. Azeotropic Boiling Temperatures (T_{az}) and Compositions (x_1^{az}) of the Binary System Pentan-1-ol (1) + Pentyl Acetate (2)

P/kPa	T_{az}/K	x_1^{az}
26.66	374.3	0.694
53.33	392.4	0.862

weighing. The uncertainties in obtaining a boiling temperature, pressure, and liquid mole fraction were estimated to be less than 0.05 K, 13 Pa, and $5\cdot10^{-4}$, respectively.

■ RESULTS AND DISCUSSION

The experimental $T-x$ equilibrium data for the binary system pentan-1-ol + pentyl acetate at pressures (26.66, 53.33, 79.99, and 101.32) kPa are reported in Table 2 and presented in Figure 1.

The $T-x$ data in binary systems were fitted with the Wilson model,[13] defined in the form

$$\ln \gamma_i = -\ln(x_i - \Lambda_{ik}x_k) + x_k\left[\frac{\Lambda_{ik}}{x_i + \Lambda_{ik}x_k} - \frac{\Lambda_{ki}}{x_k + \Lambda_{ki}x_i}\right] \qquad (1)$$

where γ_i is the activity coefficient of component i in the liquid phase.

The Wilson parameters each of four experimental pressures are presented in Table 3.

Additionally Table 3 contains the standard deviation and mean relative error of pressure calculation.

Standard deviations σP were calculated by

$$\sigma P = \left[\sum^{N} (P_{\text{calc}} - P_{\text{expt}})^2/(N - n)\right]^{1/2} \qquad (2)$$

Table 6. Experimental Vapor−Liquid Equilibria Data for the Ternary System Pentan-1-ol (1) + Pentyl Acetate (2) + Nonane (3) at Four Pressures and Values Calculated by the Wilson Equation (eq 6): Activity Coefficients (γ_1, γ_2, and γ_3), Vapor Mole Fractions (y_1 and y_2), Excess Gibbs Energy (G^E), Pressure (P_{calc}), and Differences in Pressure ($\Delta P = P_{calc} - P_{expt}$) [a]

experimental data			calculated values							
x_1	x_2	T_{expt}/K	γ_1	γ_2	γ_3	y_1	y_2	G^E/J·mol^{-1}	P_{calc}/kPa	ΔP/kPa
					P/kPa = 26.66					
0.123	0.123	371.58	2.778	1.256	1.066	0.286	0.113	623.9	26.57	−0.09
0.425	0.426	371.99	1.236	1.057	1.902	0.449	0.336	648.1	26.55	−0.12
0.118	0.235	372.38	2.449	1.169	1.109	0.248	0.206	649.0	26.87	0.20
0.267	0.534	372.86	1.419	1.019	1.599	0.335	0.417	610.8	26.70	0.04
0.184	0.368	371.72	1.842	1.058	1.267	0.286	0.288	739.3	26.56	−0.11
0.137	0.726	375.47	1.530	1.005	1.538	0.207	0.614	377.7	26.84	0.17
0.267	0.466	372.05	1.481	1.022	1.513	0.338	0.356	698.1	26.61	−0.05
0.424	0.152	369.20	1.454	1.067	1.484	0.462	0.108	1031.7	26.64	−0.03
0.234	0.117	369.77	2.115	1.151	1.159	0.382	0.092	884.4	26.56	−0.10
0.429	0.215	369.59	1.384	1.056	1.575	0.455	0.155	961.1	26.51	−0.15
0.587	0.294	371.70	1.122	1.127	2.303	0.552	0.243	625.2	26.71	0.04
0.747	0.126	370.95	1.062	1.213	2.738	0.640	0.109	608.5	26.82	0.16
0.437	0.281	370.22	1.315	1.053	1.691	0.454	0.207	869.4	26.51	−0.15
0.262	0.369	371.14	1.598	1.037	1.395	0.344	0.277	798.7	26.53	−0.14
0.578	0.133	369.36	1.217	1.094	1.888	0.529	0.098	949.1	26.73	0.06
0.228	0.659	374.59	1.394	1.015	1.673	0.301	0.543	446.7	26.89	0.22
0.488	0.269	370.42	1.248	1.068	1.830	0.482	0.201	838.8	26.67	0.01
0.676	0.108	369.76	1.124	1.143	2.249	0.580	0.084	826.5	26.84	0.17
0.250	0.250	370.31	1.798	1.074	1.269	0.357	0.189	873.0	26.45	−0.21
0.672	0.219	371.63	1.082	1.176	2.565	0.605	0.188	590.4	26.82	0.15
0.151	0.566	373.64	1.669	1.019	1.390	0.230	0.455	563.0	26.73	0.07
					P/kPa = 53.33					
0.123	0.123	392.03	2.509	1.154	1.049	0.301	0.107	544.4	53.44	0.10
0.425	0.426	391.16	1.187	1.028	1.802	0.480	0.323	560.2	53.00	−0.33
0.118	0.235	392.77	2.256	1.112	1.079	0.266	0.201	555.2	52.63	0.30
0.267	0.534	392.64	1.337	1.006	1.510	0.357	0.414	531.2	53.38	0.05
0.184	0.368	391.81	1.735	1.036	1.206	0.310	0.287	646.2	53.20	−0.13
0.137	0.726	395.66	1.402	1.002	1.448	0.215	0.618	323.4	53.38	0.05
0.267	0.466	391.88	1.402	1.007	1.427	0.364	0.352	613.8	53.38	0.04
0.424	0.152	388.24	1.408	1.017	1.409	0.502	0.103	945.6	53.47	0.14
0.234	0.117	389.39	1.978	1.077	1.128	0.409	0.087	797.3	53.31	−0.03
0.429	0.215	388.67	1.341	1.015	1.488	0.495	0.148	873.6	53.17	−0.16
0.587	0.294	390.43	1.097	1.072	2.168	0.591	0.226	540.9	53.39	0.05
0.747	0.126	389.26	1.052	1.119	2.516	0.686	0.097	548.4	53.68	0.34
0.437	0.281	389.20	1.273	1.016	1.594	0.492	0.198	781.7	52.87	−0.46
0.262	0.369	390.85	1.519	1.015	1.321	0.373	0.273	707.7	53.10	−0.23
0.578	0.133	387.98	1.193	1.034	1.767	0.575	0.091	873.9	53.45	0.12
0.228	0.659	394.53	1.295	1.006	1.586	0.315	0.540	377.8	53.68	0.34
0.488	0.269	389.31	1.213	1.026	1.721	0.522	0.191	753.3	53.23	−0.10
0.676	0.108	388.04	1.110	1.068	2.083	0.628	0.076	761.2	53.36	0.03
0.250	0.250	389.99	1.707	1.037	1.215	0.388	0.184	778.0	53.06	−0.28
0.672	0.219	390.12	1.065	1.102	2.392	0.647	0.170	515.0	53.59	0.26
0.151	0.566	393.99	1.554	1.012	1.308	0.246	0.460	488.6	53.54	0.20
					P/kPa = 79.99					
0.123	0.123	405.43	2.287	1.160	1.043	0.297	0.110	512.6	80.08	0.08
0.118	0.235	406.19	2.066	1.114	1.073	0.263	0.205	528.8	80.54	0.54
0.267	0.534	405.46	1.282	1.000	1.484	0.363	0.413	487.5	79.77	−0.23
0.184	0.368	404.93	1.631	1.034	1.194	0.312	0.289	611.7	79.88	−0.12

Table 6. Continued

experimental data			calculated values							
x_1	x_2	T_{expt}/K	γ_1	γ_2	γ_3	y_1	y_2	G^E/J·mol^{-1}	P_{calc}/kPa	ΔP/kPa
0.137	0.726	408.95	1.320	1.000	1.430	0.215	0.622	296.3	80.13	0.13
0.267	0.466	404.77	1.344	1.000	1.403	0.371	0.352	570.6	80.02	0.02
0.424	0.152	400.59	1.379	1.001	1.367	0.521	0.101	895.6	80.10	0.10
0.234	0.117	402.34	1.871	1.079	1.112	0.415	0.088	750.1	80.07	0.07
0.429	0.215	401.09	1.313	0.997	1.445	0.513	0.145	824.3	79.78	−0.22
0.587	0.294	402.72	1.086	1.040	2.089	0.611	0.216	493.0	80.25	0.25
0.747	0.126	401.06	1.050	1.064	2.401	0.709	0.090	518.7	80.34	0.34
0.437	0.281	401.60	1.248	0.998	1.548	0.509	0.194	732.1	79.22	−0.78
0.262	0.369	403.76	1.453	1.009	1.300	0.381	0.274	664.7	79.77	−0.23
0.578	0.133	400.14	1.184	1.000	1.695	0.599	0.087	832.3	80.30	0.30
0.228	0.659	407.51	1.236	1.002	1.558	0.319	0.541	337.8	80.24	0.24
0.488	0.269	401.66	1.193	1.002	1.666	0.541	0.185	704.4	79.84	−0.16
0.676	0.108	399.98	1.106	1.021	1.987	0.653	0.072	727.9	80.01	0.01
0.250	0.250	402.88	1.625	1.034	1.196	0.395	0.185	734.3	79.66	−0.34
0.672	0.219	402.11	1.059	1.058	2.294	0.669	0.161	473.9	80.23	0.23
0.151	0.566	407.19	1.460	1.010	1.295	0.247	0.463	459.8	80.27	0.27
					P/kPa = 101.32					
0.123	0.123	413.85	2.206	1.128	1.040	0.298	0.108	488.6	101.62	0.29
0.118	0.235	414.54	2.005	1.087	1.068	0.266	0.202	496.5	101.78	0.45
0.184	0.368	413.16	1.612	1.019	1.175	0.321	0.287	573.8	101.16	−0.17
0.137	0.726	417.13	1.336	1.000	1.348	0.224	0.622	279.5	101.24	−0.09
0.267	0.466	412.77	1.344	0.996	1.353	0.383	0.351	542.3	101.23	−0.10
0.424	0.152	408.37	1.374	0.980	1.342	0.534	0.098	870.4	101.86	0.52
0.234	0.117	410.37	1.833	1.051	1.104	0.422	0.086	722.4	101.51	0.18
0.429	0.215	408.78	1.311	0.983	1.411	0.527	0.142	798.5	101.07	−0.27
0.587	0.294	410.21	1.089	1.042	1.980	0.625	0.214	489.4	101.57	0.24
0.747	0.126	408.35	1.053	1.058	2.314	0.722	0.088	516.4	101.68	0.35
0.437	0.281	409.31	1.248	0.990	1.499	0.524	0.192	708.9	100.38	−0.95
0.262	0.369	411.78	1.445	0.999	1.270	0.392	0.271	630.7	100.97	−0.36
0.578	0.133	407.58	1.186	0.983	1.650	0.614	0.084	816.7	101.59	0.25
0.228	0.659	415.60	1.248	1.004	1.459	0.330	0.539	330.3	101.87	0.53
0.488	0.269	409.22	1.196	0.996	1.607	0.556	0.183	685.4	100.87	−0.46
0.676	0.108	407.39	1.109	1.005	1.928	0.668	0.070	719.6	101.48	0.15
0.250	0.250	410.86	1.604	1.015	1.181	0.404	0.182	699.9	100.76	−0.57
0.672	0.219	409.51	1.063	1.059	2.186	0.682	0.159	472.1	101.61	0.27
0.151	0.566	415.49	1.460	1.004	1.253	0.256	0.463	425.7	101.56	0.23

[a] The mean relative absolute difference (δP) is 0.345.

where P_{calc} and P_{expt} are the calculated and experimental values of the total pressure, respectively, N is the number of experimental points, and n is the number of parameters in correlation models.

The mean relative error δP between experimental and calculated pressure is defined as:

$$\delta P = \frac{1}{N}\sum^{N} |(P_{expt} - P_{calc})/P_{expt}| \cdot 100 \qquad (3)$$

The saturated vapor pressures of pure components P_i^0 were calculated by the Antoine equation

$$\ln(P_i^0/\text{kPa}) = A_i - \frac{B_i}{T/\text{K} + C_i} \qquad (4)$$

The coefficients A_i, B_i, and C_i are reported in Table 4.

The experimental VLE data indicate the existence of a minimum boiling azeotrope in the binary system pentan-1-ol + pentyl acetate at the pressures (26.66 and 53.33) kPa but did not at the higher pressures. Holley[9] showed that the system forms an azeotrope at the pressure 102.66 kPa; Lewell and Kristmanson[8] indicated that the system is nonazeotropic at the pressure 100.765 kPa. Berg et al.[14] found also that the system is nonazeotropic at the pressure 101.32 kPa.

The azeotropic points have been determined from the function

$$\alpha_{12} = \frac{y_1/y_2}{x_1/x_2} \qquad (5)$$

where y_i is the mole fraction of component i in the vapor phase, calculated by the Wilson equation and solving for $\alpha_{12} = 1$.

Azeotropic parameters at pressures (26.66 and 53.33) kPa for the system pentan-1-ol + pentyl acetate are presented in Table 5.

The isobaric VLE data for the ternary system are given in Table 6. Experimental $T-x$ are presented together with calculated values of

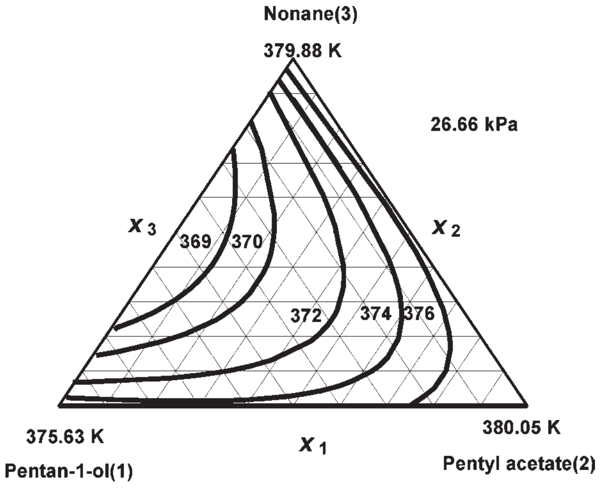

Figure 2. Boiling temperature isotherms calculated by the Wilson equation[13] for pentan-1-ol (1) + pentyl acetate (2) + nonane (3) at 26.66 kPa. Bold lines in Gibbs triangle: isotherms at (369, 370, 372, 374, and 376) K.

activity coefficients, vapor compositions, excess Gibbs energy, and total pressures predicted by the Wilson equation. For example, the values of activity coefficients in the ternary systems can be calculated from eq 6.

$$\gamma_i = \exp\left[1 - \ln\left(\sum_{j=1}^{3} x_j \Lambda_{ij}\right) - \sum_{k=1}^{3} \frac{x_k \Lambda_{ki}}{\sum_{j=1}^{3} x_j \Lambda_{kj}}\right] \qquad (6)$$

In Figure 2, the predicted boiling temperature isotherms for the ternary system at 26.66 kPa are presented on the Gibbs triangle. However, all of the binaries form at 26.66 kPa the minimum boiling azeotropes (pentan-1-ol + pentyl acetate (Table 5), pentan-1-ol + nonane,[3] pentyl acetate + nonane[6]), and quite a considerable deviation from Raoult's law exists, but the ternary system does not exhibit an azeotropic behavior.

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