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Isobaric Vapor−Liquid Equilibria of the Ternary System Methylbutyl Ketone + 1-Pentanol + Nonane

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Isobaric vapor−liquid equilibria (VLE) were determined for the ternary system methylbutyl ketone + 1-pentanol + nonane and for the binaries methylbutyl ketone + 1-pentanol and 1-pentanol + nonane. Measurements were made in a semi-microebulliometer at the pressures of (26.66, 53.33, and 79.99) kPa. A minimum boiling azeotrope was observed in the 1-pentanol + nonane system. The Wilson and modified Wilson models were used to correlate the binary VLE data. The VLE data of the ternary system were predicted by the modified Wilson model.

Introduction

This work is a part of a continuing study of thermodynamic properties of ternary ketone-containing mixtures. In the previous papers of this series, we have presented experimental results on isobaric vapor−liquid equilibrium (VLE) and molar excess enthalpies (H^E) for the two ternary systems methylbutyl ketone (hexan-2-one) + *o*-xylene + nonane,[1,2] and methylbutyl ketone + cyclohexanol + nonane.[3,4] Only H^E results were reported for the following ketone-containing ternary systems: *o*-xylene + methylbutyl ketone + cyclohexanol,[4] *p*-xylene + methylbutyl ketone + pentyl ethanoate,[5] and cyclohexanone + pentyl ethanoate + *p*-xylene.[5] Such thermodynamic information is important for immediate application to practical engineering problems and can be used to test and develop models for correlation and prediction of thermodynamic properties of mixtures.

In the present work, isobaric VLE data have been obtained at pressures of (26.66, 53.33 and 79.99) kPa for the ternary system methylbutyl ketone + 1-pentanol + nonane and for two constituent binaries containing 1-pentanol. No data for VLE of these systems have been found in the literature. However, Seymour and Carmichael,[6] Roekens and Verhoeye,[7] and Kushner et al.[8] reported data on the azeotropic parameters for 1-pentanol + nonane at 101.32 kPa. For methylbutyl ketone + nonane, our VLE data have been published earlier.[1] The modified Wilson model[9] with linear temperature-dependent parameters was used to correlate the binary VLE data and to predict the ternary system. For comparison, the VLE data in the binary systems were fitted with Wilson model[10] as well.

The modified Wilson model includes the parameters $A_{ij} = \exp(a_{ij} + b_{ij}/T)$ and avoids using the ratio of molar volumes V_j/V_i. Therefore, for correlating binary VLE, four parameters (a_{12}, b_{12}, a_{21}, b_{21}) are needed, guaranteeing in most cases a more exact description of nonideal systems. Evidently, for prediction VLE in ternary systems, values of 12 parameters (4 × 3) must be available from the binary mixtures.

Experimental Section

Materials. Nonane and methylbutyl ketone used for the present measurements were the same as in our earlier works.[1,3] Both substances were twice fractionally distilled in a Teflon spinning band column. The samples were collected and stored under argon in glass ampules. Purity, checked by gas chromatography, was greater than 99.5 % (methylbutyl ketone) and 99.8 % (nonane). 1-Pentanol of 99.5 % purity was dried with CaO and distilled at atmospheric pressure on the same column. The final GLC purity was greater than 99.7 %. Densities, refractive indices, and normal boiling temperatures were measured and compared with the literature values in Table 1.

Table 1. Densities (ρ) and Refractive Indices (n_D) at 293.15 K and Normal Boiling Temperatures (T_b) of Pure Components

	ρ/kg·m^{-3}		n_D		T_b/K	
component	exptl	lit	exptl	lit	exptl	lit
methylbutyl ketone	811.2	811.3[b]	1.4008	1.4007[b]	400.69	400.35[a]
nonane	717.6	717.6[c]	1.4055	1.4054[b]	423.97	423.95[a]
1-pentanol	814.5	814.8[a]	1.4098	1.4100[a]	410.79	410.95[a]

[a] Ref 11. [b] Ref 12. [c] Ref 13.

Apparatus and Procedure. The boiling temperature−liquid composition ($T-x$) results were obtained at constant pressure in a semi-microebulliometer. The detail description of the apparatus and procedure has been reported previously.[14,15] Boiling temperature of liquid was measured by a specially manufactured thermistor. The pressures were determined using a well-type mercury manometer. The liquid mixtures were prepared by mass. The uncertainties in the boiling temperature, pressure and liquid mole fraction were estimated to be less than 0.05 K, 13.33 Pa, and 5 × 10^{-4}, respectively.

Results and Discussion

The experimental $T-x$ equilibrium data for binary systems methylbutyl ketone + 1-pentanol and 1-pentanol + nonane at pressures of (26.66, 53.33 and 79.99) kPa are reported in Table 2. The boiling temperature−composition diagram for the binaries at used pressures are presented in Figure 1 and Figure 2. Solid lines showed the calculated (by the modified Wilson equation) boiling temperature versus liquid-phase mole fraction of the first component. The calculated vapor-phase composition is also presented on Figure 1 and Figure 2. The vapor phase was calculated, considering the ideal behavior of the vapor.

The $T-x$ data of the binary systems were fitted with the two-parameter Wilson model[10] and by our modified Wilson model.[9]

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Table 2. Isobaric Vapor−Liquid Equilibrium Data: Liquid Phase Mole Fraction (x_1) and Boiling Temperatures (T) in Binary Systems

x_1	T/K at P/kPa 26.66	 53.33	 79.99
	Methylbutyl Ketone (1) + 1-Pentanol (2)		
0.000	375.63	392.70	403.80
0.179	370.46	388.78	400.55
0.284	368.18	387.02	398.97
0.394	366.13	385.17	397.37
0.531	364.11	383.40	395.85
0.669	362.37	381.99	394.78
0.803	361.02	380.76	393.64
0.900	360.11	380.01	392.98
1.000	359.51	379.52	392.57
	1-Pentanol (1) + Nonane (2)		
0.000	379.88	401.28	415.26
0.100			406.20
0.174	370.44	390.30	403.20
0.258	369.43	388.66	401.37
0.367	368.81	387.60	399.87
0.493	368.52	387.01	399.01
0.672	368.97	387.17	398.93
0.790	369.93	388.02	399.73
0.894	372.03	389.82	401.24
1.000	375.63	392.70	403.80

The parameters of both models were calculated as unified values for all boiling temperatures at each of three experimental pressures and are presented in Table 3 for binary systems containing 1-pentanol studied here and for methylbutyl ketone + nonane investigated earlier.[1] Additionally Table 3 contains standard deviation and mean relative error of pressure calculation.

Standard deviations (σP) were calculated by

$$\sigma P = [\sum^{N}(P_{\text{calcd}} - P_{\text{exptl}})^2/(N - n)]^{1/2} \qquad (1)$$

where P_{calcd} and P_{exptl} 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 ($n = 2$ by Wilson model, $n = 4$ by modified Wilson model).

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

$$\delta P = \frac{1}{N}\sum^{N}|(P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}}| \times 100 \qquad (2)$$

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

$$\ln(P_i^0/\text{kPa}) = A_i - \frac{B_i}{T/\text{K} + C_i} \qquad (3)$$

The coefficients A, B, and C determined for 1-pentanol in this work and those for methylbutyl ketone[1] and nonane,[5] are reported in Table 4.

The experimental VLE data indicate the existence of a minimum boiling azeotrope for two binary systems containing nonane. Azeotropic data for 1-pentanol+ nonane were determined from the function

$$\alpha_{12} = \frac{y_1/y_2}{x_1/x_2} \qquad (4)$$

where y_i is the mole fraction of component i in the vapor phase calculated by the modified Wilson equation.

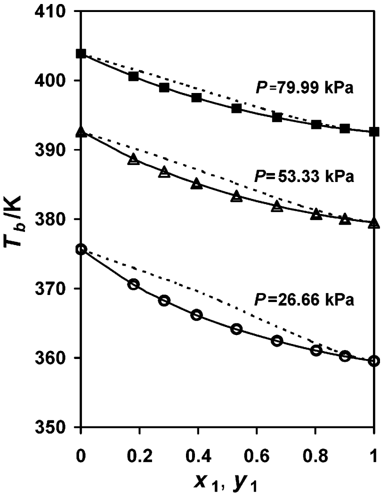

Figure 1. Experimental boiling temperature $T_b - x_1$ diagrams for methylbutyl ketone + 1-pentanol at pressures: ○, 26.66 kPa; △, 53.33 kPa; and ■, 79.99 kPa. Calculated by the modified Wilson equation[9] curves: $T_b - x_1$ (solid lines), $T_b - y_1$ (dotted lines).

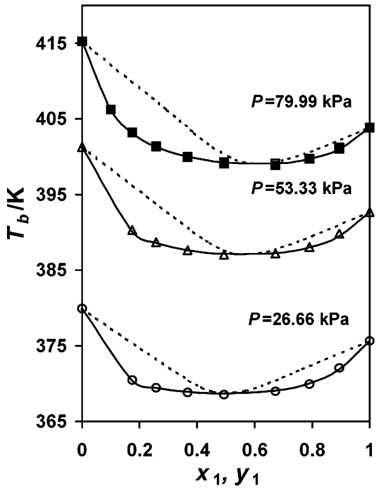

Figure 2. Experimental boiling temperature $T_b - x_1$ diagrams for 1-pentanol + nonane at pressures: ○, 26.66 kPa; △, 53.33 kPa; and ■, 79.99 kPa. Calculated by the modified Wilson equation[9] curves: $T_b - x_1$ (solid lines), $T_b - y_1$ (dotted lines).

Table 3. Values of $(\lambda_{ij}-\lambda_{ii})/R$ (the Wilson Equation[10]), a_{ij}, b_{ij} (the Modified Wilson Equation[9]), and Standard Deviations (σP; eq 1) and Mean Relative Errors (δP; eq 2) of Calculated Pressure for Binary Systems

	1-pentanol (1) + nonane (2)	methylbutyl ketone (1) + nonane (2)[a]	methylbutyl ketone (1) + 1-pentanol (2)
	Wilson Equation		
$(\lambda_{12}-\lambda_{11})/R/(\text{J·mol}^{-1})$	4548	1532	−565.9
$(\lambda_{21}-\lambda_{22})/R/(\text{J·mol}^{-1})$	537	1074	1577
σP/kPa	0.628	0.335	0.435
δP/0.01	1.15	0.482	0.859
	Modified Wilson Equation		
a_{12}	3.5350	1.70016	0.12214
b_{12}/K	−1790.89	−728.735	−51.474
a_{21}	−0.1213	−1.03432	1.66968
b_{21}/K	−180.67	−155.70	−764.49
σP/kPa	0.292	0.193	0.139
δP/0.01	0.333	0.220	0.174

[a] Ref 1.

Azeotropic data at pressures of (26.66, 53.33, and 79.99) kPa for this system, solving for $\alpha_{12} = 1$, are presented in Table 5 together with azeotropic points at 101.32 kPa from the

Table 4. Coefficients for the Antoine Vapor−Pressure Equation (eq 3)

component	A_i	B_i	C_i
methylbutyl ketone	14.0050	3104.454	−69.962
1-pentanol	13.4704	2442.413	−139.0184
nonane	13.8546	3224.816	−74.824

Table 5. Azeotropic Boiling Temperatures (T_{az}) and Compositions (x_1^{az}) of the Binary System 1-Pentanol (1) + Nonane (2) versus Pressure (P)

P/kPa	T_{az}/K	x_1^{az}
26.66	368.5	0.505
53.33	386.9	0.563
79.99	398.8	0.605
101.32		0.6580 [6]
101.32	405.89 [7]	0.6298 [7]
101.32	404.45 [8]	0.6242 [8]

literature.[6−8] Azeotropic data of methylbutyl ketone + nonane have been reported by us earlier.[1] The binary system methylbutyl ketone + 1-pentanol is nonazeotropic and has a positive deviation from ideal behavior. As seen from Table 3, the modified Wilson model gives better results in correlation of binaries in comparison with the Wilson model[10] and, therefore, has been used for prediction of ternary VLE. Experimental isobaric $T-x$ data and calculated values of activity coefficients, vapor compositions, Gibbs energies, pressures, and boiling temperatures for the ternary system methylbutyl ketone + 1-pentanol + nonane are presented in Table 6 together with differences between calculated and experimental pressure and boiling temperature values. The mean (absolute) differences between experimental and calculated values of pressures and of boiling temperatures were 0.47 kPa and 0.27 K, respectively; standard deviation of pressure was 0.62 kPa.

In Figure 3, the predicted boiling temperature isotherms for the ternary system methylbutyl ketone + 1-pentanol + nonane at 79.99 kPa are presented on the Gibbs triangle. As seen from Table 3 and Figure 3, a ternary azeotrope was not detected; the

Table 6. Experimental Vapor−Liquid Equilibria Data for the Ternary System Methylbutyl Ketone (1) + 1-Pentanol (2) + Nonane (3) at Three Pressures and Values Calculated by the Modified Wilson Equation[9] of Activity Coefficients (γ_1, γ_2, and γ_3), Vapor Mole Fractions (y_1 and y_2), Excess Gibbs Energy (G^E), Pressure (P_{calcd}), Boiling Temperature (T_{calcd}), and Differences in Pressure (ΔP) and Boiling Temperature (ΔT)[a]

experimental data			calculated values									
x_1	x_2	T_{exptl}/K	γ_1	γ_2	γ_3	y_1	y_2	G^E/J·mol^{-1}	P_{calcd}/kPa	ΔP/kPa	T_{calcd}/K	ΔT/K
						$P = 79.99$ kPa						
0.252	0.252	396.62	1.163	1.537	1.262	0.333	0.302	863.6	79.29	−0.69	396.89	0.27
0.397	0.398	395.11	1.062	1.165	1.796	0.456	0.340	672.0	79.67	−0.31	395.23	0.12
0.333	0.333	395.40	1.091	1.292	1.501	0.398	0.320	821.6	79.31	−0.68	395.66	0.26
0.573	0.287	394.02	1.032	1.190	1.885	0.619	0.240	512.8	79.77	−0.21	394.10	0.08
0.411	0.206	395.04	1.105	1.448	1.362	0.492	0.219	774.3	79.42	−0.56	395.26	0.22
0.135	0.271	398.06	1.221	1.654	1.192	0.196	0.370	885.3	78.89	−1.09	398.48	0.42
0.274	0.548	396.11	1.089	1.094	1.988	0.336	0.461	641.9	78.95	−1.03	396.50	0.39
0.219	0.438	396.22	1.109	1.234	1.554	0.274	0.417	875.9	78.86	−1.12	396.65	0.43
0.173	0.346	396.83	1.157	1.426	1.323	0.231	0.392	932.9	78.48	−1.50	397.41	0.58
0.201	0.533	396.55	1.104	1.141	1.762	0.252	0.474	794.3	79.06	−0.92	396.90	0.35
0.504	0.331	394.54	1.042	1.178	1.847	0.557	0.279	578.3	80.04	0.06	394.52	−0.02
0.702	0.199	393.49	1.016	1.223	1.947	0.732	0.167	383.1	80.08	0.10	393.45	−0.04
0.321	0.225	396.10	1.148	1.512	1.290	0.408	0.259	826.5	79.76	−0.19	396.19	0.07
0.604	0.132	393.77	1.054	1.397	1.505	0.661	0.128	601.6	79.80	−0.18	393.84	0.07
0.766	0.078	392.98	1.020	1.356	1.706	0.792	0.071	400.2	79.95	−0.03	392.99	0.01
						$P = 53.33$ kPa						
0.252	0.252	383.74	1.183	1.593	1.288	0.345	0.286	910.2	52.69	−0.63	384.08	0.34
0.397	0.398	382.48	1.078	1.856	1.864	0.473	0.317	715.8	53.03	−0.29	382.63	0.15
0.333	0.333	382.70	1.107	1.322	1.547	0.413	0.300	867.4	52.77	−0.55	382.99	0.29
0.573	0.287	381.26	1.040	1.224	1.958	0.632	0.224	552.5	53.15	−0.17	381.35	0.09
0.411	0.206	382.09	1.116	1.507	1.396	0.503	0.206	817.2	52.82	−0.50	382.36	0.27
0.135	0.271	385.28	1.251	1.714	1.213	0.206	0.354	931.6	52.44	−0.88	385.75	0.47
0.274	0.548	383.77	1.115	1.103	2.073	0.355	0.432	681.0	52.61	−0.71	384.14	0.37
0.129	0.438	383.72	1.134	1.252	1.605	0.289	0.392	919.8	52.44	−0.88	384.18	0.46
0.173	0.346	384.29	1.183	1.460	1.355	0.243	0.371	978.9	52.30	−1.02	384.83	0.54
0.201	0.533	384.26	1.133	1.511	1.831	0.268	0.446	833.6	52.71	−0.61	384.58	0.32
0.504	0.331	381.89	1.053	1.206	1.918	0.571	0.260	620.2	53.45	0.13	381.82	−0.07
0.702	0.199	380.66	1.020	1.272	2.022	0.741	0.157	415.2	53.43	0.11	380.60	−0.06
0.321	0.225	383.16	1.157	1.571	1.318	0.419	0.244	871.9	53.04	−0.26	383.31	0.14
0.604	0.132	380.81	1.058	1.469	1.548	0.667	0.121	633.8	53.21	−0.11	380.87	0.06
0.766	0.078	380.00	1.022	1.437	1.764	0.794	0.068	420.5	53.34	0.02	379.99	−0.01
						$P = 26.66$ kPa						
0.252	0.252	364.09	1.219	1.676	1.330	0.370	0.253	973.2	26.18	−0.48	364.54	0.45
0.397	0.398	363.02	1.052	1.217	1.973	0.505	0.274	776.1	26.33	−0.33	363.33	0.31
0.333	0.333	363.19	1.136	1.368	1.619	0.440	0.261	929.5	26.21	−0.45	363.62	0.43
0.573	0.287	361.58	1.054	1.278	2.075	0.658	0.193	608.9	26.41	−0.25	361.82	0.24
0.411	0.206	362.26	1.135	1.599	1.450	0.524	0.180	876.2	26.23	−0.43	362.68	0.42
0.135	0.271	365.76	1.303	1.802	1.247	0.226	0.319	993.1	26.01	−0.65	366.37	0.61
0.274	0.548	364.63	1.160	1.116	2.210	0.392	0.378	733.9	26.08	−0.58	365.17	0.54
0.219	0.438	364.52	1.178	1.278	1.686	0.317	0.345	977.4	26.03	−0.63	365.11	0.59
0.173	0.346	364.94	1.230	1.509	1.407	0.267	0.329	1039.8	25.92	−0.74	365.63	0.69
0.201	0.533	365.17	1.183	1.166	1.939	0.298	0.393	885.5	26.11	−0.55	365.68	0.51
0.504	0.331	362.30	1.071	1.250	2.031	0.600	0.224	679.4	26.58	−0.08	362.37	0.07
0.702	0.199	360.88	1.026	1.353	2.143	0.759	0.136	461.5	26.62	−0.04	360.92	0.04
0.321	0.225	363.36	1.184	1.662	1.363	0.443	0.215	934.0	26.34	−0.32	363.67	0.31
0.604	0.132	360.93	1.065	1.589	1.619	0.681	0.106	678.6	26.54	−0.12	361.04	0.11
0.766	0.078	360.09	1.023	1.580	1.856	0.801	0.060	488.8	26.65	−0.01	360.10	0.01

[a] Mean relative absolute error of pressure (δP) is 1.00 %, and standard deviation (σP) is 0.62 kPa.

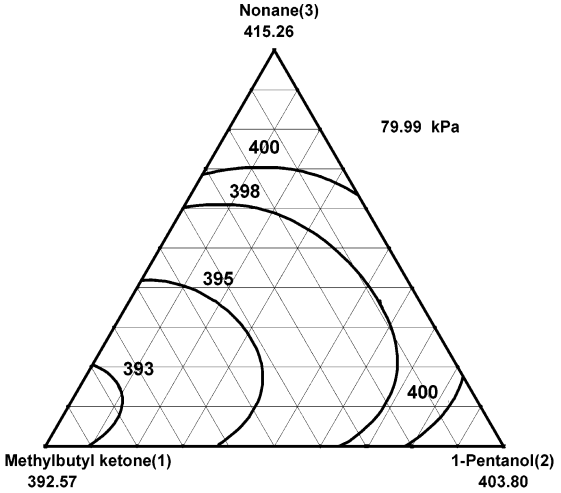

Figure 3. Calculated by the modified Wilson equation[9] boiling temperature isotherms for the ternary methylbutyl ketone (1) + 1-pentanol (2) + nonane (3) at 79.99 kPa.

ternary system is characterized by quite considerable positive deviation from ideal behavior.

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