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Isobaric Vapor−Liquid Equilibria in the System *o*-Xylene + Amyl Acetate + Nonane

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Isobaric vapor−liquid equilibria were measured for the system *o*-xylene + amyl acetate + nonane and for three constituent binary systems at the pressures 101.32, 79.99, 53.33, and 26.66 kPa. The measurements were made in a semi-microebulliometer. Nonane formed minimum boiling azeotropes with *o*-xylene and amyl acetate while the binary system *o*-xylene + amyl acetate was nonazeotropic. The Wilson model was used to correlate the binary boiling temperature (T)−composition (x) data. The $T-x$ data of the ternary system were found to be well predicted by the Wilson model, giving significantly better results than the UNIFAC method.

Introduction

In our previous papers,[1,2] excess enthalpies of ternary mixtures composed of an oxygenate compound and two hydrocarbons were reported. Empirical formulations such as the Redlich−Kister equations were examined and tested for the description of ternary mixture excess enthalpies. As a continuation of our systematic determination of thermodynamic properties of mixtures, we will report the isobaric vapor−liquid equilibrium (VLE) data for the same type of ternary system *o*-xylene + amyl acetate + nonane and its constituent binaries. This thermodynamic information is important for testing existing models or theories of mixing, for extending group contribution schemes, and for promoting a general understanding of interactions in solution.

No VLE data were found in the literature for this ternary system or for the related binaries except for *o*-xylene + nonane, for which only one set of isobaric data at a pressure of 101.32 kPa was available.[3]

VLE data obtained were used to test the Wilson model,[4] which predicts equilibrium properties of the ternary mixtures from those of the related binary mixtures. The experimental data were compared with the results obtained with the UNIFAC group contribution method[5] using the group interaction parameters from the literature.[6]

Experimental Section

Apparatus and Procedure. The $T-x$ results were obtained at constant pressure in a semi-microebulliometer. The details of the apparatus have been described previously.[7] The boiling temperature of liquid was measured by a specially manufactured thermistor.[8] In each experiment, the pressure, measured with a well-type mercury manometer with an accuracy of 13.33 Pa, was fixed and remained constant using a vacuum pump and a barostat. The heating and shaking systems of the liquid mixture were turned on. The system was kept at the boiling point at least for 15 min to ensure that the steady state was reached. The experiment was carried out at small overheating capacities of 0.8, 0.6, 0.4, and 0.2 W. After the equilibrium was achieved, the resistance of the thermistor was measured. The resistance of the thermistor corresponding to an overheating capacity of zero was found by extrapolation. The boiling temperature was calculated from the measured value of thermistor resistance, r (kΩ), by using the empirical equation

$$T^{0.9} = \frac{b}{a + \ln r} + c \qquad (1)$$

The values of the constants a, b, and c were determined from the data of cyclohexane, benzene, *m*-xylene, heptane, octane, nonane, and decane. The uncertainty in the measurement of a boiling point was estimated to be less than 0.05 K. The liquid mixtures were prepared by weighing and transferred into the equilibrium vessel by syringe. An analytical balance WA-33 (Poland) with an accuracy of 0.05 mg was used. The amount of liquid was less than 1 mL. The mole fraction composition uncertainty of a liquid mixture was estimated to be less than 5×10^{-4}.

Materials. *o*-Xylene and amyl acetate "purum" grade materials were twice fractionally distilled in a Teflon rotor column. The purity was checked by gas chromatography. All analyses were carried out on a chromatograph Chrom-5 (Czechoslovakia) provided with a flame ionization detector. The packing in the column (glass tube, i.d. = 3 mm, 2.5 m long) was Chromaton N-AW-DMCS, and the liquid phase was 5% DC-550. The purity was greater than 99.5 mass % (*o*-xylene) and 99.8 mass % (amyl acetate). Nonane "puriss" grade material was used without further purification; its purity was greater than 99.8 mass %. Densities, measured with a capillary pycnometer, and refractive indices, measured with a calibrated Abbe refractometer, thermostated within ±0.05 K, are compared in Table 1 with those reported in the literature together with normal boiling temperatures.

Results and Discussion

The liquid-phase mole fraction x_I and boiling temperature measurements at the pressures 101.32, 79.99, 53.33, and 26.66 kPa are reported in Table 2 for binary systems and in Table 3 for the ternary system. The experimental boiling temperature (T)−composition (x) measurements in binary systems were fitted with the Wilson model[4] in the form

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Table 1. Densities ρ, Refractive Indices n_D at 293.15 K, and Normal Boiling Points T_b of Pure Components

	ρ/kg·m^{-3}		n_D		T_b/K	
component	exp	lit.	exp	lit.	exp	lit.
o-xylene	880.1	880.1[a]	1.5054	1.50545[a]	417.53	417.55[b]
amyl acetate	875.4	875.3[b]	1.4027	1.4028[b]	422.59	422.35[b]
nonane	717.6	717.72[a]	1.4055	1.40542[a]	423.97	423.95[b]

[a] *TRC Thermodynamic Tables* (1996).[9] [b] Dean, 1992.[10]

Table 2. Isobaric Vapor–Liquid Equilibrium Data, Liquid Phase Mole Fraction x_1, and Boiling Temperatures T in Binary Systems

$P = 101.32$ kPa		$P = 79.99$ kPa		$P = 53.33$ kPa		$P = 26.66$ kPa	
x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K
o-Xylene (1) + Amyl Acetate (2)							
0.000	422.59	0.000	414.20	0.000	400.72	0.000	380.05
0.165	421.57	0.165	413.14	0.165	399.55	0.165	378.78
0.259	421.12	0.266	412.57	0.259	399.02	0.259	378.08
0.266	421.04	0.273	412.48	0.266	398.95	0.266	378.06
0.273	421.02	0.360	411.89	0.273	398.88	0.360	377.37
0.360	420.36	0.434	411.59	0.360	398.31	0.399	377.21
0.458	419.92	0.458	411.40	0.434	397.95	0.458	376.82
0.549	419.46	0.549	410.92	0.458	397.76	0.549	376.11
0.683	418.84	0.683	410.25	0.549	397.19	0.683	375.27
0.878	418.02	0.878	409.37	0.683	396.45	0.878	374.09
1.000	417.53	1.000	408.82	0.878	395.44	1.000	373.40
				1.000	394.86		
o-Xylene (1) + Nonane (2)							
0.000	423.97	0.000	415.26	0.000	401.28	0.000	379.88
0.099	422.67	0.099	413.93	0.099	399.93	0.099	378.52
0.200	421.36	0.200	412.65	0.200	398.67	0.200	377.22
0.292	420.39	0.292	411.69	0.292	397.72	0.292	376.26
0.317	420.26	0.317	411.54	0.317	397.55	0.317	376.12
0.598	418.20	0.598	409.51	0.449	396.36	0.449	374.99
0.816	417.47	0.816	408.77	0.598	395.53	0.598	374.15
0.897	417.34	0.897	408.65	0.790	394.77	0.790	373.41
1.000	417.53	1.000	408.82	0.816	394.79	0.897	373.27
				0.897	394.70	1.000	373.40
				1.000	394.86		
Amyl Acetate (1) + Nonane (2)							
0.000	423.97	0.000	415.26	0.000	401.28	0.000	379.88
0.098	422.07	0.098	413.43	0.098	399.52	0.098	378.31
0.204	420.73	0.204	412.09	0.204	398.29	0.204	377.14
0.293	420.02	0.293	411.38	0.293	397.74	0.293	376.67
0.386	419.52	0.386	410.96	0.386	397.25	0.386	376.29
0.512	419.22	0.512	410.71	0.512	397.08	0.512	376.18
0.594	419.22	0.594	410.75	0.594	397.16	0.594	376.32
0.709	419.59	0.709	411.12	0.709	397.60	0.709	376.76
0.800	420.17	0.800	411.70	0.800	398.21	0.800	377.42
0.901	421.16	0.901	412.74	0.901	399.27	0.901	378.47
1.000	422.59	1.000	414.20	1.000	400.72	1.000	380.05

Table 3. Isobaric Vapor–Liquid Equilibrium Data, Liquid Phase Mole Fractions x_1 and x_2, Boiling Temperature T, Calculated Vapor Mole Fractions y_1 and y_2, and Calculated Difference in Boiling Temperature ΔT for the Ternary System *o*-Xylene (1) + Amyl Acetate (2) + Nonane (3) at Pressures P

experimental			Wilson			UNIFAC		
x_1	x_2	T/K	ΔT^a/K	$y_{1,\mathrm{calc}}$	$y_{2,\mathrm{calc}}$	ΔT^a/K	$y_{1,\mathrm{calc}}$	$y_{2,\mathrm{calc}}$
$P = 101.32$ kPa								
0.400	0.399	418.55	0.04	0.413	0.373	−2.29	0.417	0.378
0.250	0.250	418.83	0.02	0.268	0.263	−1.73	0.275	0.275
0.333	0.333	418.44	0.03	0.346	0.324	−2.05	0.351	0.333
0.400	0.200	418.33	0.05	0.420	0.203	−1.76	0.418	0.219
0.250	0.499	418.86	0.04	0.261	0.471	−2.10	0.274	0.465
0.200	0.400	418.72	0.05	0.210	0.396	−1.84	0.221	0.399
0.501	0.250	418.12	0.01	0.514	0.238	−2.03	0.506	0.255
0.138	0.138	420.37	−0.11	0.161	0.170	−1.28	0.169	0.182
0.648	0.176	417.86	0.02	0.658	0.164	−1.75	0.640	0.187
0.842	0.079	417.61	0.02	0.845	0.072	−1.01	0.826	0.091
0.292	0.582	419.42	0.04	0.309	0.543	−2.29	0.327	0.528
0.128	0.291	419.21	0.06	0.140	0.316	−1.45	0.149	0.326
0.712	0.096	417.65	0.02	0.721	0.091	−1.25	0.703	0.109
0.130	0.580	419.22	−0.06	0.136	0.552	−1.83	0.150	0.542
0.754	0.164	417.86	0.05	0.763	0.150	−1.62	0.740	0.175
0.085	0.170	420.41	−0.03	0.099	0.209	−1.13	0.106	0.222
$P = 79.99$ kPa								
0.400	0.399	410.00	0.07	0.415	0.370	−2.07	0.418	0.374
0.250	0.250	410.27	0.02	0.269	0.262	−1.60	0.276	0.273
0.333	0.333	409.89	0.06	0.347	0.321	−1.87	0.352	0.330
0.400	0.200	409.77	0.04	0.422	0.201	−1.63	0.420	0.216
0.250	0.499	410.36	0.04	0.262	0.468	−1.93	0.275	0.462
0.200	0.400	410.17	0.08	0.211	0.394	−1.66	0.222	0.396
0.501	0.250	409.54	0.04	0.516	0.235	−1.83	0.508	0.252
0.138	0.138	411.67	−0.04	0.162	0.170	−1.11	0.170	0.181
0.648	0.176	409.22	0.07	0.660	0.162	−1.53	0.642	0.183
0.842	0.079	408.96	0.02	0.847	0.071	−0.89	0.829	0.089
0.292	0.582	410.91	0.06	0.311	0.540	−2.07	0.328	0.525
0.128	0.291	410.63	0.08	0.140	0.315	−1.31	0.149	0.325
0.712	0.096	408.97	0.08	0.722	0.089	−1.07	0.705	0.107
0.130	0.580	410.72	−0.04	0.137	0.550	−1.67	0.151	0.539
0.754	0.164	409.23	0.07	0.765	0.148	−1.42	0.743	0.171
0.085	0.170	411.76	−0.01	0.100	0.210	−1.00	0.107	0.221
$P = 53.33$ kPA								
0.400	0.399	396.28	0.06	0.420	0.363	−1.72	0.421	0.368
0.250	0.250	396.47	0.03	0.273	0.258	−1.33	0.279	0.270
0.333	0.333	396.13	0.07	0.351	0.316	−1.54	0.354	0.324
0.400	0.200	395.93	0.05	0.426	0.197	−1.33	0.423	0.212
0.250	0.499	396.73	0.02	0.265	0.462	−1.66	0.276	0.457
0.200	0.400	396.47	0.09	0.214	0.388	−1.40	0.223	0.392
0.501	0.250	395.74	0.02	0.520	0.230	−1.50	0.511	0.246
0.138	0.138	397.80	−0.04	0.165	0.169	−0.94	0.172	0.180
0.648	0.176	395.38	0.04	0.663	0.158	−1.23	0.647	0.177
0.842	0.079	395.03	0.01	0.848	0.069	−0.67	0.833	0.084
0.292	0.582	397.29	0.04	0.316	0.532	−1.77	0.330	0.519
0.128	0.291	396.89	0.07	0.142	0.312	−1.11	0.151	0.322
0.712	0.096	395.09	0.03	0.725	0.087	−0.85	0.709	0.103
0.130	0.580	397.10	−0.02	0.139	0.543	−1.44	0.151	0.534
0.754	0.164	395.33	0.09	0.768	0.144	−1.08	0.749	0.164
0.085	0.170	397.93	−0.01	0.102	0.209	−0.85	0.108	0.220
$P = 26.66$ kPa								
0.400	0.399	375.23	0.16	0.427	0.353	−1.24	0.427	0.357
0.250	0.250	375.37	0.12	0.278	0.253	−1.00	0.283	0.263
0.333	0.333	375.06	0.18	0.357	0.308	−1.12	0.359	0.315
0.400	0.200	374.78	0.12	0.433	0.190	−0.98	0.429	0.204
0.250	0.499	375.76	0.11	0.270	0.452	−1.25	0.280	0.447
0.200	0.400	375.47	0.18	0.217	0.381	−1.03	0.226	0.383
0.501	0.250	374.59	0.11	0.528	0.222	−1.07	0.518	0.235
0.138	0.138	376.56	0.04	0.169	0.168	−0.71	0.177	0.177
0.648	0.176	374.16	0.09	0.671	0.150	−0.84	0.655	0.167
0.842	0.079	373.69	0.03	0.853	0.065	−0.42	0.840	0.077
0.292	0.582	376.34	0.11	0.323	0.522	−1.31	0.334	0.509
0.128	0.291	375.84	0.13	0.145	0.308	−0.83	0.154	0.317
0.712	0.096	373.87	−0.01	0.731	0.082	−0.63	0.716	0.095
0.130	0.580	376.22	0.01	0.141	0.534	−1.13	0.153	0.525
0.754	0.164	374.07	0.12	0.776	0.136	−0.69	0.759	0.153
0.085	0.170	376.72	0.06	0.104	0.208	−0.62	0.111	0.218

[a] $\Delta T = T_{\mathrm{calc}} - T_{\mathrm{exp}}$.

$$\ln \gamma_1 = -\ln(x_1 - A_{12}x_2) + x_2\left[\frac{A_{12}}{(x_1 + A_{12}x_2)} - \frac{A_{21}}{(x_2 + A_{21}x_1)}\right] \tag{2}$$

$$\ln \gamma_2 = -\ln(x_2 - A_{21}x_1) + x_1\left[\frac{A_{21}}{(x_2 + A_{21}x_1)} - \frac{A_{12}}{(x_1 + A_{12}x_2)}\right] \tag{3}$$

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

The Wilson parameters (A_{jk}) were obtained by minimizing the objective function

$$F = \sum_{i=1}^{N}(P_{\mathrm{calc}} - P_{\mathrm{exp}})_i^2 \tag{4}$$

where P_{calc} and P_{exp} are the calculated and experimental values of the total pressure, respectively, and N is the number of experimental points.

The calculated vapor pressure P_{calc} was given by

Table 4. Coefficients for the Antoine Vapor Pressure Equation, Eq 6

	coefficients		
component	*A*	*B*	*C*
o-xylene	14.043 69	3352.595	−61.832
amyl acetate	14.018	3215.228	−80.532
n-nonane	13.854 59	3224.816	−74.824

Table 5. Fitted Parameters A_{12} and A_{21} for the Wilson Equation and Calculated Absolute Mean Errors δP/% at Four Pressures in kPa

system (1) + (2)	eq 2	*P* = 101.32	*P* = 79.99	*P* = 53.33	*P* = 26.66
o-xylene + amyl acetate	A_{12}	1.3902	1.2083	1.2643	0.9828
	A_{21}	0.6462	0.7821	0.7414	0.9946
	δP	0.10	0.06	0.07	0.10
o-xylene + nonane	A_{12}	1.3023	1.2903	1.3059	1.2606
	A_{21}	0.5757	0.5770	0.5515	0.5625
	δP	0.08	0.07	0.08	0.09
amyl acetate + nonane	A_{12}	0.7767	0.7578	0.7233	0.7201
	A_{21}	0.8074	0.8087	0.8211	0.7782
	δP	0.04	0.04	0.08	0.09

Table 6. Azeotropic Boiling Temperature T_{az} and Composition x^{az} of Binary Systems versus Pressure *P*

	o-xylene (1) + nonane (2)		amyl acetate (1) + nonane (2)	
P/kPa	T_{az}/K	x_1^{az}	T_{az}/K	x_1^{az}
101.32	417.3	0.897	419.2	0.538
79.99	408.6	0.900	410.7	0.524
53.33	394.7	0.905	397.0	0.507
26.66	373.2	0.910	376.1	0.489

$$P_{calc} = \sum_{i=1}^{n} P_i^{\circ} x_i \gamma_i \tag{5}$$

where *n* is the number of components and γ_i is presented by eqs 2 and 3.

The vapor pressures of pure components P_i° required were calculated with the Antoine equation

$$\ln(P_i^{\circ}/\mathrm{kPa}) = A - \frac{B}{T/K + C} \tag{6}$$

where *A*, *B*, and *C* are reported in Table 4.

Table 5 reports the A_{12} and A_{21} values of eqs 2 and 3 at each pressure together with the mean relative deviations between experimental and calculated pressure. δP/% is given by

$$\delta P = \frac{1}{N}\sum^{N} |(P_{exp} - P_{calc})/P_{exp}| \times 100 \tag{7}$$

The binary systems exhibit a slight to moderate positive deviation from ideality, and minimum boiling azeotropes were present in *o*-xylene + nonane and amyl acetate + nonane systems. The azeotropic points have been determined from the function

$$\alpha_{12} = \frac{y_1/y_2}{x_1/x_2} \tag{8}$$

where y_i is the mole fraction of vapor calculated from the Wilson equation and solving for $\alpha_{12} = 1$. Azeotropic compositions x^{az}, boiling temperatures T_{az}, and pressures are shown in Table 6.

The azeotropic parameters of *o*-xylene (1) + nonane (2) at the pressure 101.32 kPa given in the literature[11] are $x_1^{az} = 0.837$ and $T_{az} = 417.4$ K.

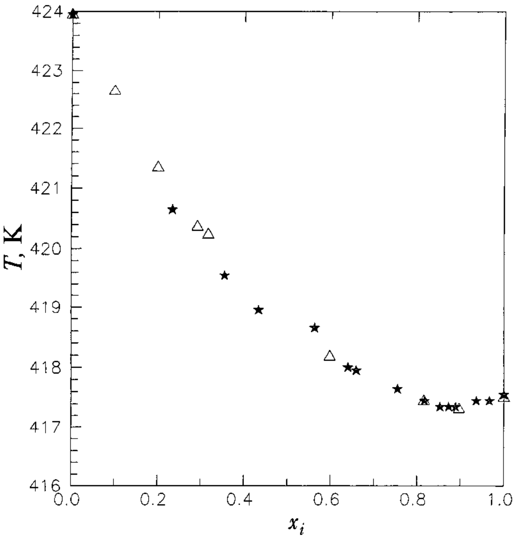

Figure 1. Temperature−composition diagram for *o*-xylene (1) + nonane (2) at 101.32 kPa: △, this work; ★, Kukharenok et al.[3]

Table 7. List of UNIFAC Group Parameters Used

A. Group of Volume and Surface Area Parameters

group	R_k	Q_k
CH_3	0.9011	0.848
CH_2	0.6744	0.540
ACH	0.5313	0.400
$ACCH_3$	1.2663	0.968
CH_3COO	1.9031	1.728

B. Interaction Parameters

	CH_2	ACH	$ACCH_3$	CH_3COO
CH_2	X	61.13	76.50	232.1
ACH	−11.12	X	167.0	5.994
$ACCH_3$	−69.70	−146.8	X	5688.0
CH_3COO	114.8	85.84	−170.0	X

As seen from Figure 1, *T*−*x* data for *o*-xylene + nonane obtained at 101.32 kPa agree satisfactorily with those reported in ref 3.

To calculate the ternary boiling temperatures and pressures, the activity coefficients for the ternary system were found from the Wilson equation

$$\ln \gamma_i = 1 - \ln(x_1A_{i1} + x_2A_{i2} + x_3A_{i3}) - \frac{x_1A_{1i}}{x_1 + x_2A_{12} + x_3A_{13}} - \frac{x_2A_{2i}}{x_1A_{21} + x_2 + x_3A_{23}} - \frac{x_3A_{3i}}{x_1A_{31} + x_2A_{32} + x_3} \tag{9}$$

where $A_{ii} = 1$.

By minimizing the objective function, eq 4, vapor pressures of pure components were expressed in P_{calc} by the Antoine equation, eq 6, where the value of *T* was the unknown.

The experimental ternary *T* data were compared with those calculated by the Wilson and UNIFAC models in Table 3. The UNIFAC group parameters used are presented in Table 7.

It is clear that the ternary data compare fairly well with those calculated with the Wilson equation and significantly worse with those calculated with the UNIFAC method. However, for the data obtained at lower pressures, this difference decreases.

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