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

Helle Kirss, Mati Kuus, and Enn Siimer*

Department of Material Science, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

Isobaric vapor−liquid equilibrium (VLE) were measured for the ternary system methylbutyl ketone + 1-pentanol + anisole and for constituent binaries methylbutyl ketone + anisole at the pressures (26.66, 53.33, 79.99, and 101.32) kPa and methylbutyl ketone + 1-pentanol at 101.32 kPa. We obtained boiling temperature−liquid composition ($T-x$) relations by using a semimicroebulliometer. The modified Wilson model with parameters that linearly depend on temperature 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 equilibrium (VLE) is important not only for testing the existing models and promoting a general understanding of interactions in solutions but also in the design of equipment for separation processes. Study of thermodynamic properties of ketone−alcohol−ether mixtures is of great industrial interest. It is known that aromatic ethers (anisole and its alkyl derivatives) can be added to gasoline as an octane number improver. Likewise, the binary alcohol−ether and alcohol−ketone mixtures are used as suitable mixed solvents.

In our previous papers, we have reported experimental results of isobaric VLE for ternary systems where the basic mixture was alkane−alcohol: nonane + cyclohexanol,[1,2] nonane + 1-pentanol.[3−5] The third component added was ketone−methylbutyl ketone[2,3] and ether−dibutyl ether[4] or anisole (methyl phenyl ether).[5]

In the present work, isobaric VLE data have been obtained at pressures of (26.66, 53.33, 79.99, and 101.32) kPa for the ternary system methylbutyl ketone + 1-pentanol + anisole and for a constituent binary methylbutyl ketone + anisole. The binary methylbutyl ketone + 1-pentanol experimental data were published at pressures of (26.66, 53.33, and 79.99) kPa.[3] In the present work, the data at pressure 101.32 kPa were supplemented. The binary 1-pentanol + anisole data were reported in our recent paper.[5]

As seen, the chosen ternary system in this work does not contain alkane, and the mixture consists of three different oxygen compounds.

No VLE data of the ternary system and the binary methylbutyl ketone + anisole have been found in the existing literature. Only Orge et al.[6] reported data for 1-pentanol + anisole at 101.32 kPa.

In many years, we have used the modified by us Wilson equation[1] to correlate binary VLE data and predict ternary VLE, which in certain cases provides the most reliable results as compared with the UNIFAC model and Wilson equation.[7] Therefore, the modified Wilson equation was also used in the present work.

* Corresponding author. E-mail: enn.siimer@staff.ttu.ee.

Table 1. Densities, ρ, 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[a]	1.4008	1.4007[a]	400.69	400.35[b]
1-pentanol	814.5	814.8[b]	1.4098	1.4100[b]	410.86	410.95[b]
anisole	994.1	994.2[b]	1.5171	1.5170[b]	426.54	426.75[c]

[a] Ref 8. [b] Ref 9. [c] Ref 10.

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

	T/K at P/kPa			
x_1	P = 26.66	P = 53.33	P = 79.99	P = 101.32
	Methylbutyl Ketone(1) + Anisole(2)			
0.000	383.10	404.24	417.99	426.54
0.218	376.15	397.22	410.82	419.30
0.294	373.89	394.81	408.27	416.72
0.418	370.65	391.45	404.90	413.29
0.488	368.96	389.72	403.17	411.48
0.598	366.56	387.17	400.50	408.82
0.701	364.73	385.12	398.43	406.63
0.799	362.83	383.12	396.27	404.51
0.900	361.02	381.16	394.27	402.46
1.000	359.51	379.52	392.57	400.69
	Methylbutyl Ketone(1) + 1-Pentanol(2)[a]			
0.000				410.86
0.151				408.31
0.271				406.72
0.358				405.65
0.511				404.10
0.686				402.45
0.896				401.07
1.000				400.69

[a] Experimental data at the pressures (26.66 kPa, 53.33 kPa, and 79.99 kPa) are reported.[3]

Experimental Section

Materials. Methylbutyl ketone, 1-pentanol, and anisole for the measurements were the same as those in our earlier works.[3−5] All substances were fractionally distilled twice in a high-efficiency Teflon spinning band (rotor) column. The samples were collected and stored under argon in glass ampules. The purity, checked by gas chromatography, was greater than 99.7 %. Densities, refractive indices, and normal boiling

10.1021/je900058p CCC: $40.75
Published on Web 04/17/2009

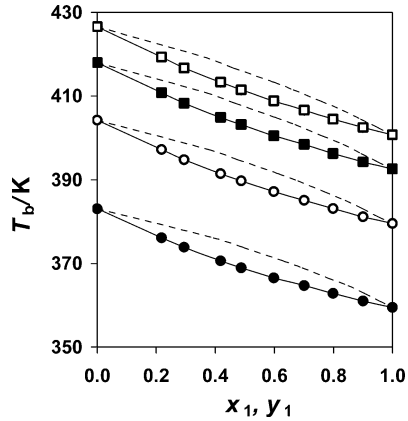

Figure 1. Experimental boiling temperature, T_b-x_1, diagrams for methylbutyl ketone (1) + anisole (2) at pressures: ●, 26.66 kPa; ○, 53.33 kPa; ■, 79.99 kPa; □, 101.32 kPa. Calculated by the modified Wilson equation curves: —, T_b-x_1; ---, T_b-y_1.

Table 3. Coefficients for the Antoine Vapor−Pressure Equation (Equation *1*)

component	A_i	B_i	C_i	temperature region, K
methylbutyl ketone[a]	14.005	3104.454	−69.963	360 to 401
1-pentanol[b]	13.2675	2277.432	−147.537	375 to 415
anisole[b]	14.2222	3418.456	−70.593	383 to 427

[a] Ref 3. [b] Ref 5.

temperatures were measured and compared with the literature values in Table 1.

Apparatus and Procedure. The boiling temperature−liquid composition ($T-x$) results were obtained at constant pressure in a semimicroebulliometer with a volume of liquid of about 1 mL. Because the vapor−liquid equilibrium apparatus in this work was the same as that used in our previous works,[1−5] only a brief description is given here. The equilibrium vessel is connected to a barostat, which keeps the pressure at the desired value with the precision of 13 Pa. The boiling temperature of the liquid was measured by a specially manufactured and calibrated thermistor. The uncertainties in the 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 values of boiling temperature measurements for the binary system methylbutyl ketone + anisole at four pressures, (26.66, 53.33, 79.99, and 101.32) kPa, and for binary system methylbutyl ketone + 1-pentanol at pressure 101.32 kPa are reported in Table 2. The $T-x$ data of the first binary system is presented in Figure 1.

The vapor pressure of pure components P_i^0 was calculated by the Antoine equation

$$\ln(P_i^0/\text{kPa}) = A_i - \frac{B_i}{T/\text{K} + C_i} \tag{1}$$

The values of A_i, B_i, and C_i and the used temperature regions are reported in Table 3.

The $T-x$ data of binary systems were fitted with the Wilson model,[7] writing

$$\ln \gamma_i = -\ln(x_i - \Lambda_{ik}x_k) + x_k\left[\frac{\Lambda_{ik}}{x_i + \Lambda_{ik}x_k} - \frac{\Lambda_{ki}}{x_k + \Lambda_{ki}x_i}\right] \tag{2}$$

where γ_i is the activity coefficient of component i in the liquid phase. We have used the modified form of the Wilson model[1]

Table 4. Values of a_{ij}, b_{ij} (the Modified Wilson Equation[1]), and Standard Deviations (σP, eq *5*) and Mean Relative Differences (δP, eq *6*) of Calculated Pressure for Binary Systems

	methylbutyl ketone(1) + 1-pentanol(2)	1-pentanol(1) + anisole(2)	methylbutyl ketone(1) + anisole(2)
a_{12}	−0.38969	1.89342	0.76211
b_{12}/K	139.934	−894.071	−114.244
a_{21}	2.32365	0.82248	−1.2565
b_{21}/K	−1009.994	−519.069	238.140
σP/kPa	0.157	0.179	0.175
$100\delta P$	0.177	0.263	0.187

considering the linear dependence of the parameters ($\Lambda_{ik} - \Lambda_{ii}$) on temperature. In this case, the coefficients Λ_{ik} and Λ_{ki} can be expressed as

$$\Lambda_{ik} = \exp\left[a_{ik} + \frac{b_{ik}}{T}\right] \tag{3}$$

$$\Lambda_{ki} = \exp\left[a_{ki} + \frac{b_{ki}}{T}\right] \tag{4}$$

including in the parameters a_{ik} and b_{ik} molar volumes of components and the gas constant. The parameters a_{ik} and b_{ik} were calculated by the Newton iteration method. Standard deviation was calculated using eq 5

$$\sigma P = \left[\sum^{N} (P_{\text{calcd}} - P_{\text{exptl}})^2/(N - n)\right]^{1/2} \tag{5}$$

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 (in determining parameters a_{ik} and b_{ik}, n is equal to 4). The mean relative difference between experimental and calculated pressure is defined as

$$\delta P = \frac{1}{N}\sum^{\text{N}} |(P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}}| \tag{6}$$

The values a_{ij} and b_{ij}, standard deviations, and mean relative errors for binary systems are reported in Table 4.

For calculation, we used all experimental data for the pressures of (26.66, 53.33, 79.99, and 101.32) kPa: for binary methylbutyl ketone (1) + 1-pentanol (2) data at (26.66, 53.33, 79.99) kPa[3] and 101.32 kPa (this work); for 1-pentanol (1) + anisole (2) data;[5] for methylbutyl ketone (1) + anisole (2) the data of this work (Table 2).

The isobaric VLE data for the ternary system are given in Table 5. Experimental $T-x$ values are presented together with calculated values of activity coefficients, vapor compositions, excess Gibbs energy (G^{E}), temperatures, and total pressures predicted by the modified Wilson equation. For example, the values of activity coefficients and the Gibbs energy (G^{E}) in ternary systems can expressed as

$$\gamma_i = \exp\left[1 - \ln(\sum_{j=1}^{3} x_j\Lambda_{ij}) - \sum_{k=1}^{3}\frac{x_k\Lambda_{ki}}{\sum_{j=1}^{3} x_j\Lambda_{kj}}\right] \tag{7}$$

where x_i is the mole fraction of component i.

$$G^{\text{E}} = -RT[\sum_{i=1}^{3} x_i \ln \sum_{j=1}^{3} x_j\Lambda_{ij}] \tag{8}$$

Comparison of experimental and calculated boiling temperatures (74 experiments) showed that the modified Wilson model

Table 5. Experimental Vapor−Liquid Data for the Ternary System Methylbutyl Ketone (1) + 1-Pentanol (2) + Anisole (3) at Four Pressures and Values Calculated by the Modified Wilson Equation[1] 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 ($\Delta P = P_{calcd} - P_{exptl}$) and Boiling Temperature ($\Delta T = T_{calcd} - T_{exptl}$)[a]

experimental data			calculated values									
x_1	x_2	T_{exptl}/K	γ_1	γ_2	γ_3	y_1	y_2	G^E/kJ·mol^{-1}	P_{calcd}/kPa	ΔP/kPa	T_{calcd}/K	ΔT/K
						$P = 26.66$ kPa						
0.728	0.136	362.7	1.002	1.446	1.064	0.824	0.108	0.182	26.56	−0.11	362.82	0.10
0.162	0.419	370.8	0.938	1.286	1.231	0.229	0.438	0.562	26.40	−0.26	371.03	0.25
0.439	0.280	367.0	0.993	1.341	1.148	0.570	0.253	0.359	26.71	0.05	366.94	−0.04
0.105	0.210	373.6	0.915	1.665	1.063	0.159	0.321	0.433	26.54	−0.12	373.75	0.12
0.274	0.549	368.5	1.056	1.124	1.420	0.402	0.450	0.433	26.49	−0.17	368.66	0.16
0.346	0.173	369.3	0.965	1.568	1.071	0.479	0.206	0.302	26.35	−0.31	369.60	0.31
0.575	0.287	364.2	1.021	1.278	1.163	0.702	0.218	0.313	26.50	−0.17	364.40	0.17
0.110	0.110	375.5	0.952	1.908	1.023	0.184	0.209	0.261	26.71	0.04	375.51	−0.04
0.312	0.312	368.9	0.969	1.356	1.160	0.426	0.314	0.432	26.47	−0.20	369.04	0.19
0.436	0.436	366.0	1.054	1.167	1.297	0.583	0.329	0.375	26.62	−0.05	366.08	0.04
0.165	0.278	371.7	0.922	1.488	1.113	0.237	0.350	0.485	26.42	−0.25	371.92	0.24
0.436	0.188	367.5	0.978	1.488	1.085	0.573	0.195	0.293	26.47	−0.20	367.72	0.20
0.630	0.123	364.7	0.994	1.511	1.056	0.756	0.112	0.183	26.65	−0.01	364.69	0.01
0.153	0.540	370.5	0.981	1.167	1.375	0.224	0.506	0.549	26.39	−0.27	370.76	0.25
0.082	0.754	371.8	1.092	1.048	1.741	0.139	0.670	0.413	26.47	−0.19	371.94	0.17
0.289	0.132	371.2	0.962	1.690	1.047	0.422	0.184	0.261	26.64	−0.03	371.27	0.03
0.263	0.474	368.9	1.006	1.190	1.316	0.373	0.419	0.479	26.46	−0.20	369.09	0.19
0.158	0.684	370.4	1.090	1.068	1.621	0.256	0.582	0.415	26.47	−0.20	370.58	0.18
0.444	0.111	368.2	0.979	1.634	1.046	0.599	0.130	0.200	26.48	−0.19	368.39	0.19
						$P = 53.33$ kPa						
0.728	0.136	382.7	1.000	1.329	1.060	0.807	0.122	0.148	53.27	−0.06	382.74	0.04
0.162	0.419	390.1	0.933	1.233	1.197	0.211	0.469	0.493	53.10	−0.23	390.16	0.12
0.439	0.280	386.7	0.986	1.268	1.130	0.541	0.280	0.304	53.51	0.18	386.56	−0.10
0.105	0.210	393.7	0.920	1.528	1.055	0.150	0.333	0.382	53.32	−0.01	393.68	0.01
0.274	0.549	387.5	1.031	1.101	1.352	0.364	0.496	0.370	53.30	−0.03	387.56	0.02
0.346	0.173	389.4	0.965	1.439	1.064	0.459	0.221	0.261	53.01	−0.33	389.62	0.18
0.575	0.287	383.8	1.011	1.216	1.142	0.671	0.248	0.258	53.06	−0.27	383.99	0.15
0.110	0.110	396.1	0.958	1.704	1.021	0.175	0.212	0.230	53.51	0.17	395.95	−0.10
0.312	0.312	388.5	0.963	1.283	1.140	0.400	0.342	0.372	53.21	−0.12	388.57	0.07
0.436	0.436	385.5	1.033	1.133	1.253	0.542	0.371	0.313	53.55	0.22	385.34	−0.12
0.165	0.278	391.4	0.923	1.391	1.098	0.222	0.370	0.426	53.06	−0.27	391.54	0.15
0.436	0.188	387.5	0.976	1.376	1.077	0.550	0.213	0.250	53.09	−0.24	387.65	0.14
0.630	0.123	384.8	0.992	1.381	1.053	0.738	0.124	0.152	53.37	0.04	384.73	−0.02
0.153	0.540	389.5	0.967	1.138	1.315	0.203	0.545	0.481	53.18	−0.15	389.56	0.08
0.082	0.754	390.2	1.058	1.040	1.605	0.121	0.712	0.362	53.41	0.07	390.13	−0.04
0.289	0.132	391.6	0.964	1.531	1.043	0.405	0.193	0.227	53.46	0.13	391.50	−0.07
0.263	0.474	388.2	0.991	1.154	1.268	0.342	0.460	0.413	53.43	0.10	388.15	−0.05
0.158	0.684	389.1	1.056	1.056	1.511	0.225	0.629	0.360	53.45	0.11	389.04	−0.06
0.444	0.111	388.5	0.980	1.479	1.043	0.579	0.140	0.172	53.14	−0.19	388.61	0.11
						$P = 79.99$ kPa						
0.728	0.136	395.7	0.998	1.261	1.057	0.798	0.128	0.125	79.79	−0.21	395.75	0.09
0.162	0.419	402.6	0.930	1.201	1.177	0.202	0.484	0.445	79.54	−0.46	402.74	0.18
0.439	0.280	399.5	0.982	1.222	1.119	0.527	0.293	0.265	80.16	0.16	399.42	−0.07
0.105	0.210	406.7	0.923	1.447	1.050	0.146	0.336	0.346	79.83	−0.17	406.80	0.07
0.274	0.549	399.9	1.016	1.087	1.312	0.345	0.520	0.326	79.81	−0.19	399.92	0.07
0.346	0.173	402.5	0.965	1.364	1.060	0.449	0.227	0.232	79.29	−0.71	402.75	0.29
0.110	0.110	409.5	0.962	1.586	1.019	0.170	0.211	0.209	80.18	0.18	409.38	− 0.07
0.312	0.312	401.2	0.960	1.239	1.127	0.387	0.354	0.331	79.66	−0.34	401.38	0.14
0.436	0.436	397.9	1.021	1.111	1.227	0.521	0.393	0.269	80.02	0.02	397.93	−0.01
0.165	0.278	404.2	0.924	1.333	1.089	0.215	0.378	0.384	79.30	−0.70	404.45	0.28
0.436	0.188	400.5	0.975	1.310	1.072	0.539	0.220	0.220	79.41	−0.59	400.70	0.24
0.630	0.123	397.8	0.992	1.305	1.051	0.729	0.130	0.131	79.90	−0.10	397.82	0.04
0.153	0.540	401.7	0.958	1.119	1.279	0.192	0.564	0.433	79.60	−0.40	401.89	0.15
0.082	0.754	402.1	1.034	1.034	1.526	0.112	0.732	0.326	80.07	0.07	402.04	−0.03
0.289	0.132	404.7	0.965	1.439	1.040	0.396	0.196	0.204	79.86	−0.14	404.76	0.06
0.263	0.474	400.6	0.981	1.132	1.239	0.326	0.479	0.367	79.90	−0.10	400.64	0.04
0.158	0.684	401.1	1.035	1.049	1.447	0.210	0.652	0.321	79.94	−0.06	401.12	0.02
0.444	0.111	401.7	0.980	1.390	1.042	0.569	0.144	0.152	79.66	−0.34	401.84	0.14
						$P = 101.32$ kPa						
0.728	0.136	403.7	0.998	1.222	1.056	0.794	0.131	0.110	100.78	−0.55	403.87	0.19
0.162	0.419	410.4	0.927	1.181	1.164	0.198	0.491	0.413	100.69	−0.65	410.63	0.21
0.439	0.280	407.4	0.980	1.195	1.113	0.519	0.299	0.241	101.19	−0.15	407.47	0.05
0.105	0.210	415.0	0.926	1.399	1.047	0.144	0.336	0.323	101.09	−0.24	415.03	0.08
0.274	0.549	407.5	1.006	1.078	1.288	0.335	0.532	0.297	100.89	−0.44	407.66	0.14
0.346	0.173	410.6	0.965	1.320	1.057	0.443	0.229	0.214	100.30	−1.04	410.96	0.35
0.110	0.110	417.9	0.964	1.518	1.018	0.168	0.208	0.195	101.71	0.38	417.78	−0.13
0.312	0.312	409.2	0.958	1.212	1.119	0.381	0.360	0.304	100.67	−0.67	409.40	0.22
0.436	0.436	405.7	1.014	1.098	1.212	0.510	0.404	0.241	101.07	−0.26	405.80	0.08
0.165	0.278	412.2	0.925	1.298	1.083	0.211	0.381	0.357	100.31	−1.02	412.55	0.34

Table 5. Continued

experimental data			calculated values									
x_1	x_2	T_{exptl}/K	γ_1	γ_2	γ_3	y_1	y_2	G^E/kJ·mol^{-1}	P_{calcd}/kPa	ΔP/kPa	T_{calcd}/K	ΔT/K
0.436	0.188	408.5	0.975	1.271	1.069	0.533	0.223	0.200	100.27	−1.07	408.86	0.36
0.630	0.123	405.9	0.991	1.262	1.050	0.724	0.132	0.118	100.71	−0.62	405.99	0.21
0.153	0.540	409.3	0.952	1.108	1.258	0.187	0.574	0.402	100.46	−0.88	409.62	0.28
0.082	0.754	409.4	1.019	1.031	1.481	0.107	0.743	0.304	101.01	−0.32	409.49	0.10
0.289	0.132	413.0	0.966	1.385	1.039	0.392	0.196	0.189	101.10	−0.24	413.05	0.08
0.263	0.474	408.3	0.975	1.119	1.222	0.318	0.490	0.337	100.85	−0.48	408.45	0.15
0.158	0.684	408.5	1.021	1.044	1.411	0.201	0.664	0.296	100.77	−0.57	408.68	0.18
0.444	0.111	409.9	0.980	1.338	1.040	0.564	0.145	0.140	100.75	−0.59	410.10	0.20

[a] Mean relative absolute difference (δP) is 0.45, standard deviation (σP) is 0.48 kPa, and mean absolute difference (ΔT) is 0.13 K.

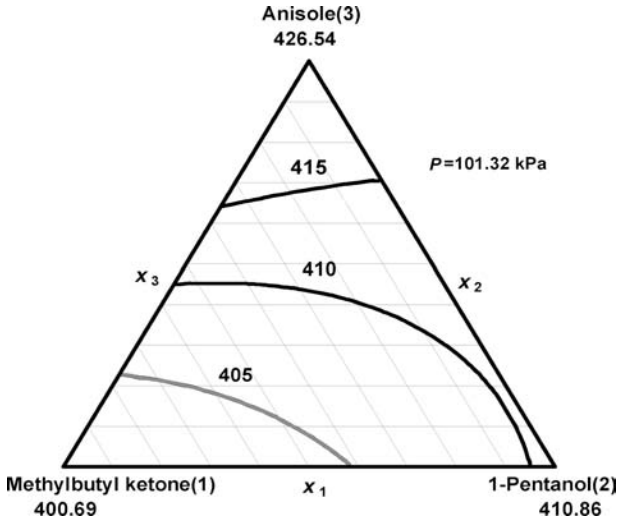

Figure 2. Boiling temperature isotherms calculated by the modified Wilson equation for methylbutyl ketone (1) + 1-pentanol (2) + anisole (3) at 101.32 kPa.

gave a good prediction for ternary system in a quite large boiling temperature region (from about (360 to 415) K). Standard deviation of pressure was calculated using eq 5, where the number of parameters was 12.

In Figure 2, the predicted boiling temperature isotherms for the ternary system methylbutyl ketone (1) + 1-pentanol (2) + anisole (3) at 101.32 kPa are presented on the Gibbs triangle. The shape of the curves indicates that the system does not exhibit an azeotropic behavior.

Literature Cited

(1) Siimer, E.; Kirss, H.; Kuus, M.; Kudryavtseva, L. Isobaric Vapor−Liquid Equilibrium for the Ternary System *o*-Xylene + Nonane + Cyclohexanol. *J. Chem. Eng. Data* **2002**, *47*, 52–55.
(2) Kirss, H.; Kuus, M.; Siimer, E. Isobaric Vapor−Liquid Equilibria of the Ternary System Methylbutyl Ketone + Nonane + Cyclohexanol. *J. Chem. Eng. Data* **2005**, *50*, 309–311.
(3) Kirss, H.; Siimer, E.; Kuus, M. Isobaric Vapor−Liquid Equilibria of the Ternary System Methylbutyl Ketone + 1-Pentanol + Nonane. *J. Chem. Eng. Data* **2006**, *51*, 153–156.
(4) Kirss, H.; Kuus, M.; Siimer, E. Isobaric Vapor−Liquid Equilibria of the Ternary System Dibutyl Ether + 1-Pentanol + Nonane. *J. Chem. Eng. Data* **2006**, *51*, 1887–1891.
(5) Kirss, H.; Kuus, M.; Siimer, E. Isobaric Vapor−Liquid Equilibria of the Ternary System 1-Pentanol + Nonane + Anisole. *J. Chem. Eng. Data* **2008**, *53*, 310–314.
(6) Orge, B.; Foco, G.; Brignole, E. Vapor−Liquid Equilibria of the Binary System 1-Pentanol + Anisole and the Quaternary System Benzene + Cyclohexane+ 1-Pentanol + Anisole at 101.32 kPa. *J. Chem. Eng. Data* **2004**, *49*, 872–875.
(7) Wilson, G. M. Vapor−Liquid Equilibrium. XI. A New Expression for Excess Free Energy of Mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127–130.
(8) *CRC Handbook of Chemistry and Physics*, 78th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1997.
(9) Dean, J. *Lange's Handbook of Chemistry*, 14th ed.; McGraw-Hill: New York, 1992.
(10) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed.; Wiley-Interscience: New York, 1986.

Received for review January 15, 2009. Accepted March 18, 2009.

JE900058P