Isobaric vapour–liquid equilibria of the ternary system hexan-2-one + *o*-xylene + nonane

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Abstract. Boiling temperatures (T) vs liquid-phase mole fractions (x) were measured for the system hexan-2-one + *o*-xylene + nonane and for two constituent binaries containing hexan-2-one at pressures 26.66, 53.33, 79.99, and 101.32 kPa. Hexan-2-one formed minimum boiling azeotrope with nonane while the binary system hexan-2-one + *o*-xylene was nonazeotropic. The modified Wilson model was used to correlate the binary T–x data and to predict vapour–liquid equilibria in the ternary system. The excess Gibbs energy calculated by the modified Wilson model and experimental H^E data at 318.15 K of the ternary system are treated simultaneously.

INTRODUCTION

As a continuation of our systematic determination of thermodynamic properties of ternary systems composed of an oxygenated compound and two hydrocarbons, vapour–liquid equilibria (VLE) data were investigated in the present study for hexan-2-one + *o*-xylene + nonane at four constant pressures (26.66, 53.33, 79.99, and 101.32 kPa). In our previous papers [1, 2], excess enthalpies (H^E) for this system at temperatures 318.15 and 298.15 K were reported. No VLE data were found in the literature [3, 4] for the ternary system mentioned and for two constituent binaries containing hexan-2-one. For the *o*-xylene + nonane isobaric VLE data have been reported earlier [5, 6].

The Wilson equation is known to be widely used for the representation of the VLE data in a variety of completely miscible mixtures. However, its reliability can be significantly increased by considering accurately the temperature dependence of the parameters.

The modified Wilson model with linear temperature dependent binary parameters [7] was applied to correlate the binary VLE data, to predict those for the ternary system, and to connect the VLE and H^E data obtained at largely different temperatures. By this model the excess Gibbs energy in the ternary system was calculated at a temperature of 318.15 K, at which H^E data were measured earlier [1].

EXPERIMENTAL

All the substances used for the present measurements were the same as in our earlier work [1]. Normal boiling temperatures, densities measured in a capillary pycnometer, and refractive indices measured in an Abbé refractometer at 293.15 K are compared with literature data in Table 1.

The boiling temperature (T) vs liquid-phase mole fractions (x) results were obtained with the semi-micro ebulliometer described in detail in [10]. Uncertainties of the boiling temperatures were estimated to be less than 0.05 K. Uncertainties of the mole fractions of a liquid mixture (x) were estimated to be less than 5×10^{-4}.

RESULTS AND DISCUSSION

The liquid-phase mole fraction and boiling temperature measurements at different pressures are reported in Table 2 for the binary systems hexan-2-one + o-xylene and hexan-2-one + nonane, and in Table 3 for the ternary system.

The T–x data in the binary systems were fitted with the Wilson model [11] in the form

$$\ln \gamma_1 = -\ln (x_1 - \Lambda_{12} x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21} x_1} \right], \qquad (1)$$

$$\ln \gamma_2 = -\ln (x_2 - \Lambda_{21} x_1) + x_1 \left[\frac{\Lambda_{21}}{x_2 + \Lambda_{21} x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} \right], \qquad (2)$$

Table 1. Normal boiling temperatures (T), densities (ρ), and refractive indices (n_D) of pure components at 293.15 K

Component	T, K		ρ, kg m^{-3}		n_D	
	Exp	Lit	Exp	Lit	Exp	Lit
Hexan-2-one	400.69	400.35[a]	811.2	811.3[b]	1.4007	1.4007[b]
o-Xylene	417.53	417.55[a]	880.1	880.2[a]	1.5054	1.5054[a]
Nonane	423.97	423.95[a]	717.6	717.6[a]	1.4055	1.4054[a]

[a] Dean, 1992 [8];
[b] Lide, 1997 [9].

Table 2. Isobaric vapour–liquid equilibria data, liquid-phase mole fraction (x_1), and boiling temperatures (T) in binary systems

x_1	T, K at pressures P, kPa			
	26.66	53.33	79.99	101.32
Hexan-2-one(1) + o-xylene(2)				
0.000	373.40	394.86	408.82	417.53
0.105	370.95	392.12	405.97	414.59
0.207	368.77	389.75	403.44	411.95
0.319	366.81	387.59	401.16	409.60
0.386	365.81	386.52	400.01	408.38
0.522	364.06	384.57	397.91	406.23
0.604	363.07	383.51	396.71	405.08
0.704	362.07	382.35	395.57	403.81
0.806	361.12	381.32	394.47	402.65
0.896	360.38	380.50	393.61	401.77
1.000	359.51	379.52	392.57	400.69
Hexan-2-one(1) + nonane(2)				
0.000	379.88	401.28	415.26	423.97
0.105	373.14	394.45	408.41	417.23
0.193	368.70	390.05	403.98	412.64
0.303	365.59	386.48	400.19	408.70
0.404	363.71	384.45	397.89	406.33
0.503	362.18	382.65	396.03	404.35
0.591	361.29	381.57	394.93	403.22
0.712	360.24	380.45	393.63	401.81
0.773	359.93	380.07	393.20	401.39
0.827	359.59	379.56	392.82	400.97
0.864	359.48	379.53	392.68	400.83
0.902	359.42	379.35	392.59	400.73
1.000	359.51	379.52	392.57	400.69

Table 3. Experimental vapour–liquid equilibria data (mole fractions in liquid phase x_i, boiling temperature T_{exp}) for the ternary system hexan-2-one(1) + o-xylene(2) + nonane(3) and mole fractions (y_i) of components in the vapour phase calculated using the modified Wilson equation, activity coefficients (γ_i), boiling temperature (T_{calc}), and total pressure (P_{calc})

Experimental data			Calculated values						
x_1	x_2	T_{exp}, K	T_{calc}, K	P_{calc}, kPa	y_1	y_2	γ_1	γ_2	γ_3
$P = 26.66$ kPa									
0.333	0.334	365.33	365.39	26.61	0.502	0.257	1.218	1.022	1.227
0.250	0.250	366.66	366.89	26.45	0.445	0.208	1.363	1.048	1.111
0.400	0.400	364.51	364.64	26.54	0.544	0.298	1.129	1.017	1.375
0.201	0.399	367.86	368.05	26.49	0.361	0.342	1.322	1.035	1.136
0.125	0.125	371.14	371.07	26.73	0.311	0.129	1.646	1.118	1.023
0.333	0.334	365.27	365.38	26.56	0.502	0.257	1.218	1.022	1.227
0.756	0.122	360.70	360.66	26.70	0.811	0.083	1.028	1.074	1.776
0.125	0.750	369.99	370.00	26.66	0.217	0.669	1.195	1.004	1.296

Table 3 continued

Experimental data			Calculated values						
x_1	x_2	T_{exp}, K	T_{calc}, K	P_{calc}, kPa	y_1	y_2	γ_1	γ_2	γ_3
0.250	0.500	367.16	367.11	26.71	0.397	0.406	1.208	1.014	1.247
0.400	0.200	364.00	364.08	26.59	0.579	0.148	1.226	1.028	1.216
0.400	0.200	364.01	364.08	26.60	0.579	0.148	1.226	1.028	1.216
0.500	0.250	362.94	363.02	26.59	0.636	0.177	1.119	1.025	1.387
			$P = 53.33$ kPa						
0.333	0.334	386.04	386.13	53.18	0.493	0.260	1.201	1.022	1.197
0.250	0.250	387.54	387.85	52.82	0.431	0.210	1.326	1.045	1.096
0.400	0.400	385.10	385.26	53.06	0.539	0.302	1.123	1.017	1.326
0.201	0.399	388.87	389.08	52.99	0.350	0.345	1.290	1.033	1.119
0.125	0.125	392.27	392.43	53.08	0.291	0.129	1.556	1.108	1.020
0.333	0.334	385.99	386.13	53.10	0.493	0.260	1.201	1.022	1.197
0.756	0.122	380.89	380.81	53.47	0.810	0.084	1.027	1.075	1.686
0.125	0.750	391.12	391.16	53.27	0.213	0.673	1.183	1.004	1.258
0.250	0.500	388.04	388.01	53.38	0.390	0.410	1.193	1.014	1.214
0.400	0.200	384.66	384.71	53.25	0.570	0.150	1.208	1.029	1.187
0.400	0.200	384.64	384.71	53.22	0.570	0.150	1.208	1.029	1.187
0.500	0.250	383.39	383.47	53.20	0.631	0.180	1.113	1.026	1.338
			$P = 79.99$ kPa						
0.333	0.334	399.60	399.69	79.78	0.488	0.263	1.190	1.021	1.179
0.250	0.250	401.16	401.56	79.08	0.423	0.212	1.302	1.044	1.087
0.400	0.400	398.50	398.73	79.46	0.536	0.304	1.118	1.017	1.297
0.201	0.399	402.58	402.82	79.44	0.344	0.347	1.270	1.031	1.108
0.125	0.125	406.25	406.38	79.69	0.279	0.129	1.502	1.102	1.018
0.333	0.334	399.52	399.69	79.59	0.488	0.263	1.190	1.021	1.179
0.756	0.122	394.04	393.97	80.17	0.809	0.085	1.027	1.075	1.631
0.125	0.750	404.94	404.97	79.93	0.210	0.675	1.175	1.004	1.235
0.250	0.500	401.65	401.67	79.95	0.385	0.413	1.183	1.013	1.196
0.400	0.200	398.14	398.20	79.86	0.565	0.152	1.196	1.028	1.170
0.400	0.200	398.09	398.20	79.74	0.565	0.152	1.196	1.028	1.170
0.500	0.250	396.75	396.84	79.80	0.628	0.181	1.108	1.026	1.308
			$P = 101.32$ kPa						
0.333	0.334	408.03	408.16	100.96	0.485	0.264	1.183	1.021	1.168
0.250	0.250	409.69	410.12	100.14	0.418	0.213	1.287	1.043	1.082
0.400	0.400	406.94	407.14	100.77	0.534	0.306	1.115	1.017	1.279
0.201	0.399	411.12	411.40	100.55	0.339	0.348	1.258	1.030	1.102
0.125	0.125	415.03	415.10	101.15	0.272	0.129	1.471	1.099	1.017
0.333	0.334	407.91	408.16	100.63	0.485	0.264	1.183	1.021	1.169
0.756	0.122	402.22	402.17	101.48	0.809	0.086	1.026	1.074	1.598
0.125	0.750	413.53	413.58	101.19	0.208	0.677	1.169	1.004	1.222
0.250	0.500	410.16	410.19	101.24	0.382	0.415	1.176	1.013	1.184
0.400	0.200	406.50	406.62	100.98	0.561	0.153	1.189	1.028	1.160
0.400	0.200	406.47	406.62	100.89	0.561	0.153	1.189	1.028	1.160
0.500	0.250	405.05	405.18	100.97	0.627	0.183	1.105	1.026	1.290

where γ_i is the activity coefficient of component i in the liquid phase and Λ_{ij} are expressed as

$$\Lambda_{12} = \exp\left[a_{12} + \frac{b_{12}}{T}\right], \tag{3}$$

$$\Lambda_{21} = \exp\left[a_{21} + \frac{b_{21}}{T}\right], \tag{4}$$

including in the parameters a_{ij} and b_{ij} the molar volumes of the components and the gas constant [7]. The parameters a_{ij} and b_{ij} were calculated by the Newton iteration method.

The prediction of vapour–liquid equilibria in the ternary system was realized on the basis of binary parameters

$$\gamma_i = \exp\left[1 - \ln B_i - \left(\frac{x_i}{B_i} + \frac{x_j \Lambda_{ji}}{B_j} + \frac{x_k \Lambda_{ki}}{B_k}\right)\right], \tag{5}$$

where γ_i is the activity coefficient of component i in the ternary mixture of the composition x_i, x_j, x_k, and

$$B_i = x_i + x_j \Lambda_{ij} + x_k \Lambda_{ik}. \tag{6}$$

Table 4 contains the correlation results of $T–x$ for binary systems containing hexan-2-one studied here and for o-xylene + nonane investigated earlier [6].

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

$$\ln(P_i^0(\text{kPa})) = A_i - \frac{B_i}{T(\text{K}) + C_i}. \tag{7}$$

The values of coefficients A_i, B_i, and C_i are reported in Table 5.

Two binary systems containing nonane exhibit minimum boiling azeotropes. Azeotropic conditions have to obey to the following relationships:

$$y_i - x_i = 0 \tag{8}$$

and

$$(\partial T / \partial x)_p = 0, \tag{9}$$

where y_i is the mole fraction of the component i in the vapour phase.

The azeotropic compositions for hexan-2-one + nonane were determined from the function

$$\alpha_{12} = \frac{y_1 / y_2}{x_1 / x_2} \tag{10}$$

Table 4. Fitted coefficients (a_{ij}, b_{ij}) of the modified Wilson equation (Eqs. 3, 4) and calculated absolute mean error (ΔP), and standard deviation (δP) of pressure for binary systems

System (1) + (2)	a_{12}	b_{12}	a_{21}	b_{21}	ΔP, %	δP, kPa
Hexan-2-one + o-xylene	1.10492	−459.039	−1.22053	436.718	0.10	0.72
Hexan-2-one + nonane	1.70016	−728.735	−1.03432	155.701	0.22	1.40
o-Xylene + nonane	0.14382	41.904	0.23169	−315.517	0.09	0.08

Table 5. Coefficients for the Antoine vapour pressure equation $\ln(P_i^0 \text{ (kPa)}) = A_i - B_i /(T(\text{K}) + C_i)$ (Eq. 7)

Component	Coefficient		
	A_i	B_i	C_i
Hexan-2-one	14.00501	3104.454	−69.962
o-Xylene	14.04369	3352.595	−61.832
Nonane	13.85459	3224.816	−74.824

solving for $\alpha_{12} = 1$, where y_i was calculated by the modified Wilson model. As an example, Fig. 1 presents an $\alpha_{12} - x_i$ diagram of the system hexan-2-one(1) + nonane(2) at four pressures.

Azeotropic compositions and boiling temperatures at four pressures for the system hexan-2-one + nonane are presented in Table 6. Azeotropic parameters of o-xylene + nonane have been reported earlier [6].

The isobaric VLE data for the ternary system calculated by the modified Wilson equation together with experimental results are given in Table 3. Comparison of experimental and calculated boiling temperatures and total pressures showed that the modified Wilson model gave a good prediction for the ternary system hexan-2-one + o-xylene + nonane in a quite large boiling temperature region (360–415 K). The mean difference (absolute) between the pressures used in the experiments and calculated pressures was 0.26 kPa, and between experimentally determined and calculated boiling temperatures 0.126 K. These differences were calculated analogously; Eq. 11 shows the calculation for the mean temperature difference

$$\Delta(T(\text{K})) = \frac{1}{N} \sum_{i=1}^{N} |T_{i,\text{exp}} - T_{i,\text{calc}}|, \tag{11}$$

where N is the number of experimental points.

Table 6. Azeotropic boiling temperature (T_{az}) and composition (x_i^{az}) versus pressure of the system hexan-2-one(1) + nonane(2)

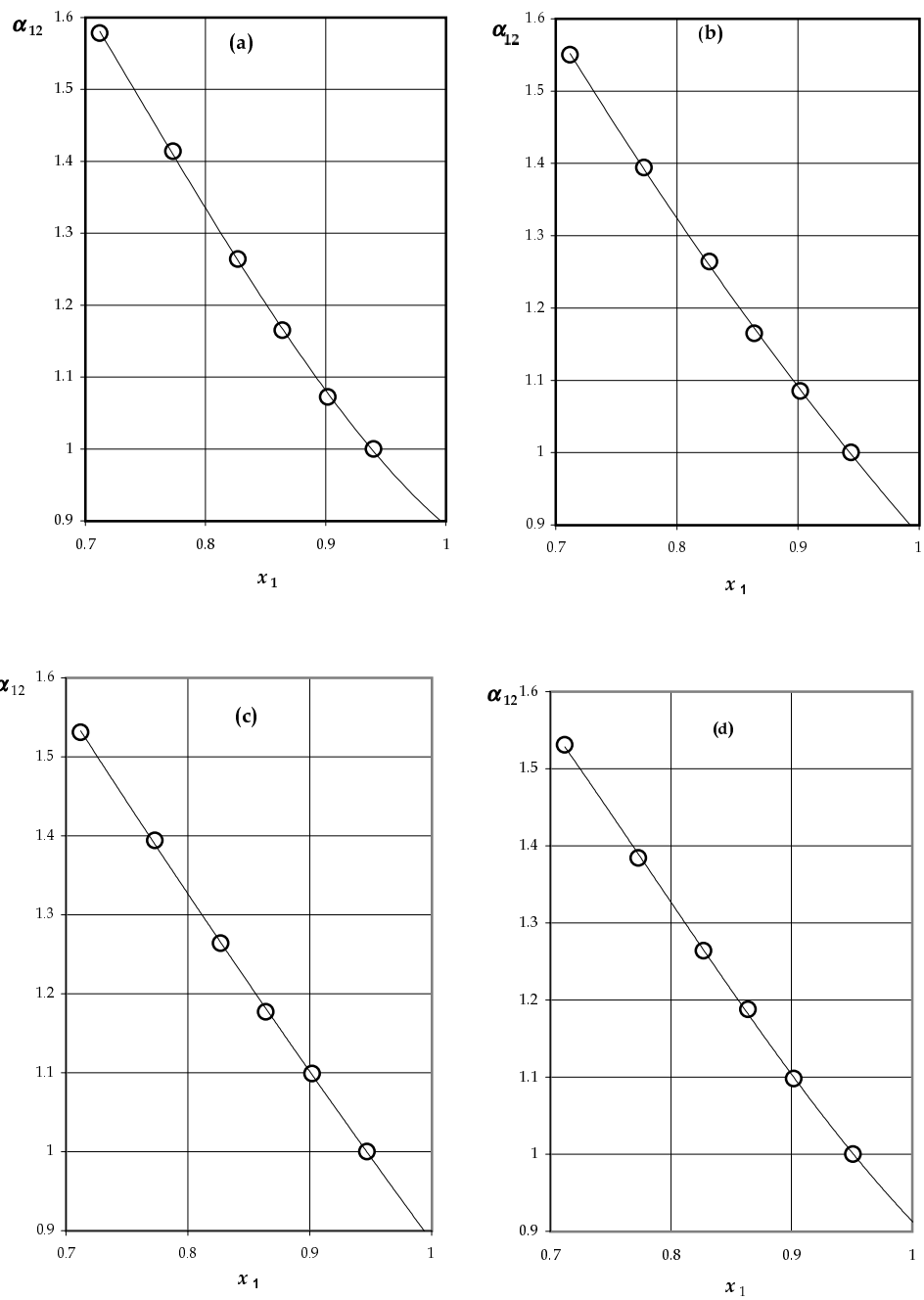| P, kPa	T_{az}, K	x_i^{az}
101.32	400.6	0.951
79.99	392.5	0.947
53.33	379.3	0.944
26.66	359.4	0.940

Fig. 1. $\alpha_{12} - x_1$ diagram of the system hexan-2-one(1) + nonane(2) at four pressures: a – 26.66, b – 53.33, c – 79.99, and d – 101.32 kPa.
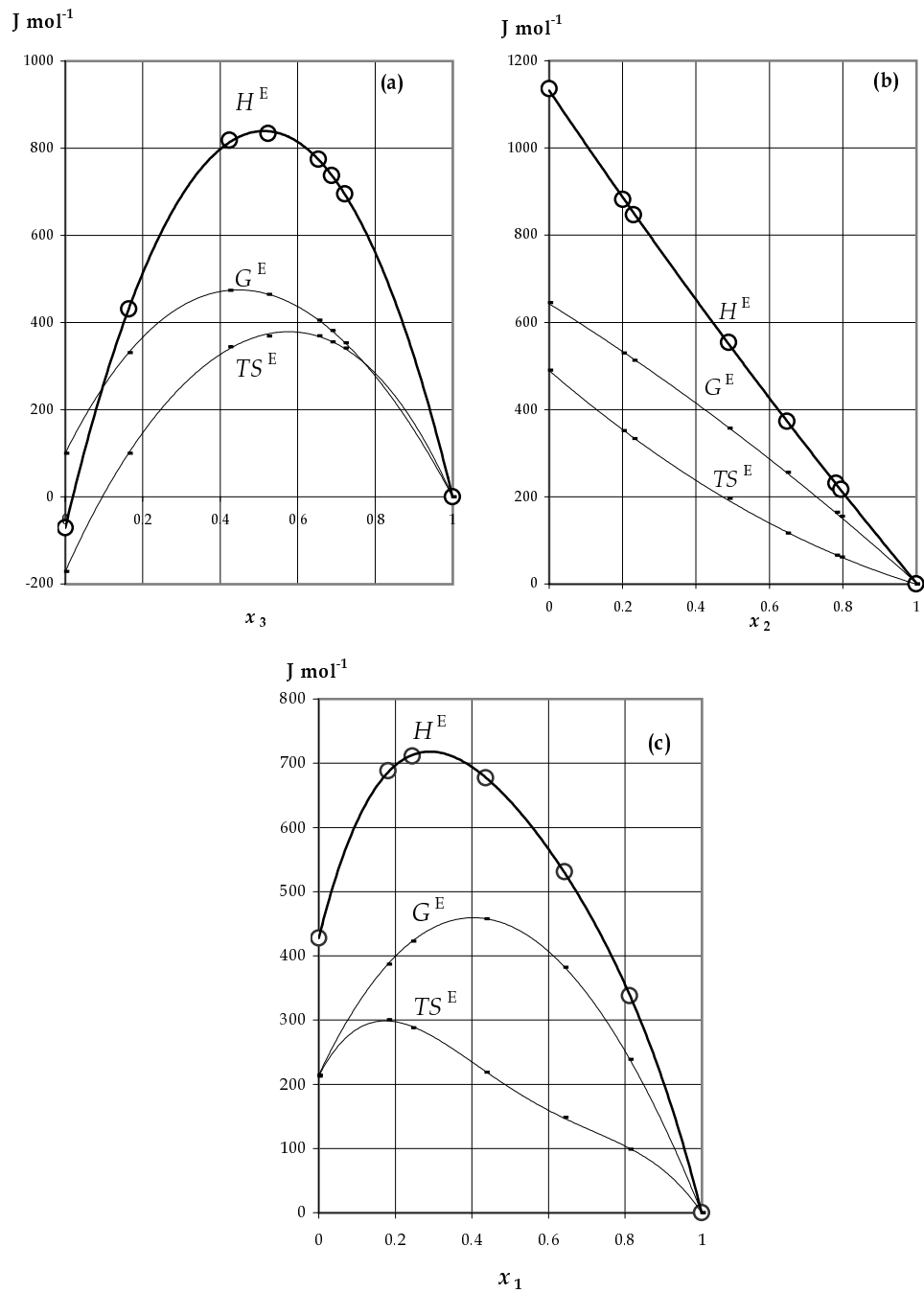
Fig. 2. Excess enthalpy, H^E, Gibbs energy, G^E, and TS^E values (J mol^{-1}) at different compositions of the ternary system hexan-2-one(1) + o-xylene(2) + nonane(3) at 318.15 K: a – $x_1/x_2 = 1$, b – $x_1/x_3 = 1$, c – $x_2/x_3 = 1$. For H^E the experimental data [1] (○) and smoothed curves are given; G^E values are calculated by the modified Wilson model [7], and TS^E values are calculated from the difference $TS^E = H^E - G^E$.

The prediction results imply that the modified Wilson equation predicts satisfactorily VLE behaviour for the ternary system also at 318.15 K. In Fig. 2 the calculated values of excess molar Gibbs free energy, G^E, are shown together with experimental values of excess molar enthalpy, H^E, of the ternary mixture at 318.15 K [1] for the molar ratio of the two components x_i/x_j equal to 1. The excess entropy term TS^E calculated from the well-known relation $TS^E = H^E - G^E$ is also shown in Fig. 2.

In all three cases the positive excess molar enthalpy is larger than G^E and TS^E, which are also positive at most compositions of the ternary system. Only in the vicinity of the binary system hexan-2-one + o-xylene H^E and TS^E are negative, and the order of the excess functions changes from $H^E > G^E > TS^E$ to $G^E > H^E > TS^E$.

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Kolmiksüsteemi heksaan-2-oon + *o*-ksüleen + nonaan isobaariline auru ja vedeliku tasakaal

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Sõltuvalt vedelfaasi koostisest (*x*) mõõdeti süsteemi heksaan-2-oon + *o*-ksüleen + nonaan ja kahe heksaan-2-ooni sisaldava binaarse süsteemi keemistemperatuuri (*T*) rõhul 26,66, 53,33, 79,99 ja 101,32 kPa. Heksaan-2-oon moodustas nonaaniga keemistemperatuuri miinimumiga aseotroobi, binaarne süsteem heksaan-2-oon + *o*-ksüleen oli mitteaseotroopne. Binaarseid *T–x* andmeid korreleeriti modifitseeritud Wilsoni võrrandiga, mida kasutati samuti auru ja vedeliku tasakaalu ennustamiseks kolmiksüsteemis. Kolmiksüsteemile 318,15 K juures saadud liigentalpia andmeid vaadeldi koos sama temperatuuri jaoks ennustatud Gibbsi liigenergia väärtustega.