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Isothermal vapour–liquid equilibrium for 1-propanol + *tert*-butanol + acetonitrile + benzene

Isamu Nagata [a]*, Andrzej Książczak [b]

[a] *Department of Chemistry and Chemical Engineering, Division of Physical Sciences, Kanazawa University, 40-20, Kodatsuno 2-chome, Kanazawa, Ishikawa 920, Japan*
[b] *Department of Physical Chemistry, Warsaw University of Technology, 00-664 Warsaw, Poland*

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Abstract

Vapour–liquid equilibrium results are presented for 1-propanol + *tert*-butanol + acetonitrile + benzene at 60°C, measured using a modified Boublik vapour-recirculating still. The experimental values agree satisfactorily with those predicted by the UNIQUAC association-solution model with binary parameters alone.

Keywords: Association; Isothermal; Quaternary system; Vapor recirculating still; UNIQUAC; VLE

1. List of symbols

a_{IJ}	binary interaction energy parameter for the $I-J$ pair
A, B, C, D	1-propanol, *tert*-butanol, acetonitrile and benzene
A_iB_jC, A_iB_jD	complexes containing i molecules of alcohol A, j molecules of alcohol B and one molecule of component C or D
A_iC, A_iD	complexes containing i molecules of alcohol A and one molecule of component C or D
B_{IJ}	second virial coefficient for the $I-J$ pair

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* Corresponding author.

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B_iC, B_iD	complexes containing i molecules of alcohol B and one molecule of component C and D
F	objective function as defined by Eq. (24)
h_{AB}, h_{AC}, h_{AD}, h_{BC}, h_{BD}	enthalpies of complex formation between unlike molecules
K_I	association constant of pure alcohol I
K_{AB}, K_{AC}, K_{AD}, K_{BC}, K_{BD}	equilibrium constants of complex formation between unlike molecules
P	total pressure
P_I^s	saturated vapour pressure of pure component I
q_I	molecular geometric-area parameter of pure component I
R	universal gas constant
r_I	molecular geometric-size parameter of pure component I
$\bar{S}_A$, $\bar{S}_B$	sums as defined by Eqs. (19) and (20)
S_A, S_B	sums as defined by Eqs. (21) and (22)
T	absolute temperature
v_I^L	molar liquid volume of pure component I
V	true molar volume of alcohol mixture
V_I^0	true molar volume of pure alcohol I
x_I	liquid-phase mole fraction of component I
y_I	vapour-phase mole fraction of component I
Z	lattice coordination number equal to 10

1.1. Greek letters

γ_I	activity coefficient of component I
θ_I	area fraction of component I
σ_P, σ_T, σ_x, σ_y	standard deviations in pressure, temperature, liquid-phase mole fraction and vapour-phase mole fraction
τ_{IJ}	$\exp(-a_{IJ}/T)$
ϕ_I	fugacity coefficient of component I at P and T
ϕ_I^s	fugacity coefficient of pure component I at P_I^s and T
Φ_I	segment fraction of component I
Φ_{I_1}	monomer segment fraction of component I
$\Phi_{I_1}^0$	monomer segment fractions of pure alcohol I

1.2. Subscripts

A, B, C, D	alcohols and active non-associating components
A_1, B_1, C_1, D_1	monomers of components A, B, C and D
A_i, B_i	i-mers of alcohols A and B
AB, AC, AD, BC, BD	binary complexes

I, J, K	components I, J and K
i, j, k, l	i, j, k and l-mers of alcohols or indices

1.3. Superscipt

*	reference state of 50°C or calculated value

2. Introduction

Previous papers from this laboratory have reported measurements of isothermal vapour–liquid equilibria (VLE) for five quaternary mixtures [1–6]. As an extension of those studies, this paper presents isothermal VLE data for 1-propanol + *tert*-butanol + acetonitrile + benzene at 60°C and the experimental values are compared with those calculated from the UNIQUAC associated-solution model with only binary parameters [7, 8]. The following VLE data for binary mixtures making up the quaternary mixture are available from the literature and are used to obtain the binary energy parameters of the model: 1-propanol + *tert*-butanol at 40°C [9]; 1-propanol + acetonitrile at 55°C [10]; 1-propanol + benzene at 45°C [11]; *tert*-butanol + acetonitrile at 60°C [12]; *tert*-butanol + benzene at 45°C [13]; acetonitrile + benzene at 45°C [14].

3. Experimental

tert-Butanol (2-methyl-2-propanol), acetonitrile and 1-propanol (Wako Pure Chemical Industries Ltd., guaranteed reagent grade) were used without further purification. Benzene (first grade) was purified by repeated recrystallization. The densities of the compounds used for experimental work, measured with an Anton Paar densimeter (DMA40) at 25°C or 30°C, agreed excellently with published values [15]. Experimental VLE data were obtained using a modified Boublik vapour-recirculating still [16]. The compositions of the liquid- and vapour-phase samples in equilibrium were analysed using a Shimadzu gas chromatograph GC-7A and a Shimadzu Chromatopac E-1B. The possible experimental errors of the measured variables are: 0.16 Torr for pressure; 0.05°C for temperature; 0.002 for liquid- and vapour-phase mole fractions.

Table 1 shows the experimental VLE data, the activity coefficients γ_I and the fugacity coefficients ϕ_I derived from the thermodynamic equations

$$\gamma_\text{I} = P\phi_I y_I / \{x_I P_I^\text{s} \phi_I^\text{s} \exp[v_I^\text{L}(P - P_I^\text{s})/RT]\} \tag{1}$$

$$\ln \phi_I = \left(2 \sum_J y_J B_{IJ} - \sum_I \sum_J y_I y_J B_{IJ}\right) \frac{P}{RT} \tag{2}$$

where P is the total pressure, P^s the pure-component vapour pressure, x the liquid-phase mole fraction, y the vapour-phase mole fraction, T the absolute temperature, v^L the pure-liquid molar volume estimated from a modified Rackett

Table 1
Quaternary experimental vapour–liquid equilibrium data for 1-propanol(1) + *tert*-butanol(2) + acetonitrile(3) + benzene(4) at 60°C

No.	x_1	x_2	x_3	x_4	y_1	y_2	y_3	y_4	P/Torr	γ_1	γ_2	γ_3	γ_4	ϕ_1	ϕ_2	ϕ_3	ϕ_4
1	0.280	0.261	0.111	0.348	0.119	0.192	0.180	0.509	440.6	1.209	1.107	1.965	1.652	0.973	0.972	0.952	0.983
2	0.411	0.133	0.089	0.367	0.183	0.097	0.149	0.571	420.0	1.211	1.048	1.945	1.675	0.976	0.973	0.957	0.983
3	0.135	0.132	0.170	0.563	0.081	0.123	0.212	0.584	476.0	1.844	1.514	1.628	1.263	0.974	0.971	0.949	0.981
4	0.138	0.657	0.033	0.172	0.057	0.509	0.076	0.385	384.8	1.023	1.023	2.453	2.061	0.971	0.975	0.958	0.987
5	0.224	0.198	0.138	0.440	0.109	0.155	0.191	0.545	452.6	1.422	1.210	1.722	1.436	0.974	0.971	0.951	0.982
6	0.284	0.260	0.221	0.235	0.126	0.194	0.306	0.374	434.5	1.243	1.107	1.643	1.783	0.972	0.971	0.945	0.989
7	0.048	0.287	0.540	0.125	0.025	0.264	0.516	0.195	459.6	1.543	1.446	1.183	1.868	0.972	0.973	0.933	0.999
8	0.154	0.475	0.138	0.233	0.060	0.344	0.216	0.380	441.0	1.105	1.091	1.889	1.850	0.969	0.971	0.947	0.986
9	0.271	0.132	0.373	0.224	0.136	0.107	0.420	0.337	442.6	1.435	1.224	1.353	1.723	0.974	0.970	0.940	0.992
10	0.256	0.340	0.288	0.116	0.110	0.263	0.404	0.223	418.1	1.159	1.106	1.596	2.087	0.973	0.973	0.942	0.996
11	0.187	0.170	0.157	0.486	0.099	0.142	0.202	0.557	463.3	1.584	1.321	1.636	1.359	0.973	0.971	0.950	0.982
12	0.172	0.234	0.215	0.379	0.083	0.184	0.261	0.472	465.6	1.448	1.249	1.543	1.488	0.972	0.970	0.945	0.982
13	0.289	0.225	0.205	0.281	0.129	0.168	0.280	0.423	441.7	1.272	1.126	1.649	1.711	0.972	0.970	0.946	0.987
14	0.140	0.507	0.243	0.110	0.055	0.382	0.355	0.208	425.0	1.074	1.095	1.689	2.084	0.970	0.973	0.941	0.994
15	0.066	0.235	0.509	0.190	0.036	0.217	0.480	0.267	469.0	1.648	1.479	1.193	1.711	0.972	0.971	0.933	0.996
16	0.069	0.453	0.065	0.413	0.029	0.345	0.103	0.523	465.4	1.258	1.212	2.030	1.507	0.970	0.972	0.953	0.980
17	0.144	0.124	0.367	0.365	0.080	0.111	0.374	0.435	478.2	1.713	1.459	1.322	1.467	0.972	0.969	0.939	0.987
18	0.133	0.386	0.335	0.146	0.056	0.300	0.402	0.242	446.5	1.210	1.186	1.452	1.919	0.970	0.972	0.938	0.994
19	0.079	0.143	0.137	0.641	0.054	0.149	0.179	0.618	474.7	2.096	1.690	1.706	1.169	0.974	0.972	0.952	0.980
20	0.178	0.604	0.079	0.139	0.069	0.461	0.169	0.301	391.1	0.976	1.023	2.303	2.185	0.970	0.974	0.953	0.989
21	0.062	0.124	0.645	0.169	0.041	0.135	0.569	0.255	464.1	1.984	1.728	1.102	1.824	0.975	0.973	0.932	0.999
22	0.197	0.210	0.152	0.441	0.096	0.167	0.202	0.535	463.3	1.457	1.258	1.689	1.439	0.973	0.971	0.949	0.982
23	0.149	0.140	0.562	0.149	0.088	0.134	0.541	0.237	446.6	1.706	1.462	1.161	1.850	0.975	0.972	0.935	0.999

equation [17], and the second virial coefficients B were estimated using the correlation of Hayden and O'Connell [18].

4. Data analysis

The UNIQUAC associated-solution model was used to analyse the experimental VLE data. We assume that in a quaternary mixture including two alcohols (A and B), acetonitrile (C) and benzene (D), alcohol molecules self-associate to form open chains A_i and B_i and then those open chains cross-associate multiply to yield open cross chains, $(A_iB_j)_k$, $(B_iA_j)_k$, $A_i(B_jA_k)_l$, and $B_i(A_jB_k)_l$. Furthermore, all these open chains produce additional chemical complexes with acetonitrile or benzene: A_iC, A_iD, B_iC, B_iD, $(A_iB_j)_kC$, $(A_iB_j)_kD$, $(B_iA_j)_kC$, $(B_iA_j)_kD$, $A_i(B_jA_k)_lC$, $A_i(B_jA_k)_lD$, $B_i(A_jB_k)_lC$, and $B_i(A_jB_k)_lD$, where the subscripts i, j, k and l range from 1 to ∞. The equilibrium constants for chemical-complex-forming reactions are assumed to be independent of the degrees of self-association and cross-association and are defined as

$$K_{\mathrm{A}} = \frac{\Phi_{\mathrm{A}_{i+1}}}{\Phi_{\mathrm{A}_i}\Phi_{\mathrm{A}_1}}\frac{i}{i+1} \quad \text{for } \mathrm{A}_i + \mathrm{A}_1 = \mathrm{A}_{i+1}$$

$$= K_{\mathrm{A}}^* \exp\left[-\frac{h_{\mathrm{A}}}{R}\left(\frac{1}{T}-\frac{1}{T^*}\right)\right] \tag{3}$$

$$K_{\mathrm{B}} = \frac{\Phi_{\mathrm{B}_{i+1}}}{\Phi_{\mathrm{B}_i}\Phi_{\mathrm{B}_1}}\frac{i}{i+1} \quad \text{for } \mathrm{B}_i + \mathrm{B}_1 = \mathrm{B}_{i+1}$$

$$= K_{\mathrm{B}}^* \exp\left[-\frac{h_{\mathrm{B}}}{R}\left(\frac{1}{T}-\frac{1}{T^*}\right)\right] \tag{4}$$

$$K_{\mathrm{AB}} = \frac{\Phi_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{B}_l}}{\Phi_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k}\Phi_{\mathrm{B}_l}}\frac{r_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k}r_{\mathrm{B}_l}}{r_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{B}_l}r_{\mathrm{A}}r_{\mathrm{B}}} \quad \text{for } \mathrm{A}_i\mathrm{B}_j\mathrm{A}_k + \mathrm{B}_l = \mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{B}_l$$

$$= \frac{\Phi_{\mathrm{B}_l\mathrm{A}_j\mathrm{B}_k\mathrm{A}_l}}{\Phi_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k}\Phi_{\mathrm{A}_l}}\frac{r_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k}r_{\mathrm{A}_l}}{r_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{A}_l}r_{\mathrm{B}}r_{\mathrm{A}}} \quad \text{for } \mathrm{B}_i\mathrm{A}_j\mathrm{B}_k + \mathrm{A}_l = \mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{A}_l$$

$$= K_{\mathrm{AB}}^* \exp\left[-\frac{h_{\mathrm{AB}}}{R}\left(\frac{1}{T}-\frac{1}{T^*}\right)\right] \tag{5}$$

$$K_{\mathrm{AC}} = \frac{\Phi_{\mathrm{A}_i\mathrm{C}}}{\Phi_{\mathrm{A}_i}\Phi_{\mathrm{C}_1}}\frac{1}{ir_{\mathrm{A}}+r_{\mathrm{C}}} \quad \text{for } \mathrm{A}_i + \mathrm{C}_1 = \mathrm{A}_i\mathrm{C}$$

$$= K_{\mathrm{AC}}^* \exp\left[-\frac{h_{\mathrm{AC}}}{R}\left(\frac{1}{T}-\frac{1}{T^*}\right)\right] \tag{6}$$

$$K_{\mathrm{BC}} = \frac{\Phi_{\mathrm{B}_i\mathrm{C}}}{\Phi_{\mathrm{B}_i}\Phi_{\mathrm{C}_1}}\frac{1}{ir_{\mathrm{B}}+r_{\mathrm{C}}} \quad \text{for } \mathrm{B}_i + \mathrm{C}_1 = \mathrm{B}_i\mathrm{C}$$

$$= K_{\mathrm{BC}}^* \exp\left[-\frac{h_{\mathrm{BC}}}{R}\left(\frac{1}{T}-\frac{1}{T^*}\right)\right] \tag{7}$$

K_{AD} and K_{BD} are similarly defined by Eqs. (6) and (7), respectively. The sizes of the chemical complexes are given as the sum of the pure-component size parameters r, e.g. $r_{A_i} = ir_A$, $r_{B_i} = ir_B$ and $r_{A_iB_j} = ir_A + jr_B$.

The activity coeffcients of 1-propanol (A) and acetonitrile (C) are expressed by

$$\ln \gamma_A = \ln\left(\frac{\Phi_{A_1}}{\Phi^0_{A_1} x_A}\right) + \frac{r_A}{V^0_A} - \frac{r_A}{V} - \left(\frac{Z}{2}\right) q_A \left(\ln \frac{\Phi_A}{\theta_A} + 1 - \frac{\Phi_A}{\theta_A}\right)$$

$$+ q_A\left[1 - \ln\left(\sum_J \theta_J \tau_{JA}\right) - \sum_J \frac{\theta_J \tau_{AJ}}{\sum_K \theta_K \tau_{KJ}}\right] \tag{8}$$

$$\ln \gamma_C = \ln \frac{\Phi_{C_1}}{x_C} + 1 - \frac{r_C}{V} - \left(\frac{Z}{2}\right) q_C \left(\ln \frac{\Phi_C}{\theta_C} + 1 - \frac{\Phi_C}{\theta_C}\right)$$

$$+ q_C\left[1 - \ln\left(\sum_J \theta_J \tau_{JC}\right) - \sum_J \frac{\theta_J \tau_{CJ}}{\sum_K \theta_K \tau_{KJ}}\right] \tag{9}$$

where Z is the coordination number set as 10, and the segment fraction Φ, the surface fraction θ, the binary adjustable parameter τ_{IJ} related to the energy parameter a_{IJ}, the pure alcohol monomer segment fraction $\Phi^0_{I_1}$ and the true molar volume V^0_I for pure alcohol I, are expressed by

$$\Phi_I = x_I r_I / \sum_J x_J r_J \tag{10}$$

$$\Phi_I = x_I q_I / \sum_J x_J q_J \tag{11}$$

$$\tau_{IJ} = \exp(-a_{IJ}/T) \tag{12}$$

$$\Phi^0_{I_1} = [2K_I + 1 - (1 + 4K_I)^{0.5}]/2K_I^2 \tag{13}$$

$$V^0_I = r_I/(1 - K_I \Phi^0_{I_1}) \tag{14}$$

The activity coefficients of *tert*-butanol (B) and benzene (D) are easily derived by changing the subscript A to B in Eq. (8) and the subscript C to D in Eq. (9). The monomer segment fractions in the mixture, Φ_{A_1}, Φ_{B_1}, Φ_{C_1}, and Φ_{D_1} are obtained from simultaneous solution of Eqs. (15)–(18)

$$\Phi_A = (1 + r_A K_{AC} \Phi_{C_1} + r_A K_{AD} \Phi_{D_1}) \bar{S}_A + \frac{r_A K_{AB} \bar{S}_A S_B}{(1 - r_A r_B K^2_{AB} S_A S_B)^2}$$

$$\times \{2 + r_B K_{AB} S_A (2 - r_A r_B K^2_{AB} S_A S_B) + r_A K_{AB} S_B$$

$$+ \Phi_{C_1}[(r_A K_{AC} + r_B K_{BC}) + r_A r_B K_{AB} K_{AC} S_A (2 - r_A r_B K^2_{AB} S_A S_B)$$

$$+ r_A r_B K_{AB} K_{BC} S_B] + \Phi_{D_1}[(r_A K_{AD} + r_B K_{BD}) + r_A r_B K_{AB} K_{AD} S_A$$

$$\times (2 - r_A r_B K^2_{AB} S_A S_B) + r_A r_B K_{AB} K_{BD} S_B]\} \tag{15}$$

$$\begin{aligned}\Phi_{\mathrm{B}} = {} & (1 + r_{\mathrm{B}}K_{\mathrm{BC}}\Phi_{\mathrm{C}_1} + r_{\mathrm{B}}K_{\mathrm{BD}}\Phi_{\mathrm{D}_1})\bar{S}_{\mathrm{B}} + \frac{r_{\mathrm{B}}K_{\mathrm{AB}}S_{\mathrm{A}}\bar{S}_{\mathrm{B}}}{(1 - r_{\mathrm{A}}r_{\mathrm{B}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}})^2} \\ & \times \{2 + r_{\mathrm{A}}K_{\mathrm{AB}}S_{\mathrm{B}}(2 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}) + r_{\mathrm{B}}K_{\mathrm{AB}}S_{\mathrm{A}} \\ & + \Phi_{\mathrm{C}_1}[(r_{\mathrm{A}}K_{\mathrm{AC}} + r_{\mathrm{B}}K_{\mathrm{BC}}) + r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}K_{\mathrm{BC}}S_{\mathrm{B}}(2 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}) \\ & + r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}K_{\mathrm{AC}}S_{\mathrm{A}}] + \Phi_{\mathrm{D}_1}[(r_{\mathrm{A}}K_{\mathrm{AD}} + r_{\mathrm{B}}K_{\mathrm{BD}}) + r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}K_{\mathrm{BD}}S_{\mathrm{B}} \\ & \times (2 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}) + r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}K_{\mathrm{AD}}S_{\mathrm{A}}]\}\end{aligned} \qquad (16)$$

$$\begin{aligned}\Phi_{\mathrm{C}} = \Phi_{\mathrm{C}_1}\Bigg\{ & 1 + r_{\mathrm{C}}K_{\mathrm{AC}}S_{\mathrm{A}} + r_{\mathrm{C}}K_{\mathrm{BC}}S_{\mathrm{B}} \\ & + \frac{r_{\mathrm{A}}r_{\mathrm{B}}r_{\mathrm{C}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}}{(1 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}})}\left[\frac{K_{\mathrm{AC}}}{r_{\mathrm{B}}K_{\mathrm{AB}}} + \frac{K_{\mathrm{BC}}}{r_{\mathrm{A}}K_{\mathrm{AB}}} + K_{\mathrm{AC}}S_{\mathrm{A}} + K_{\mathrm{BC}}S_{\mathrm{B}}\right]\Bigg\}\end{aligned} \qquad (17)$$

$$\begin{aligned}\Phi_{\mathrm{D}} = \Phi_{\mathrm{D}_1}\Bigg\{ & 1 + r_{\mathrm{D}}K_{\mathrm{AD}}S_{\mathrm{A}} + r_{\mathrm{D}}K_{\mathrm{BD}}S_{\mathrm{B}} \\ & + \frac{r_{\mathrm{A}}r_{\mathrm{B}}r_{\mathrm{D}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}}{(1 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}})}\left[\frac{K_{\mathrm{AD}}}{r_{\mathrm{B}}K_{\mathrm{AB}}} + \frac{K_{\mathrm{BD}}}{r_{\mathrm{A}}K_{\mathrm{AB}}} + K_{\mathrm{AD}}S_{\mathrm{A}} + K_{\mathrm{BD}}S_{\mathrm{B}}\right]\Bigg\}\end{aligned} \qquad (18)$$

where the sums, $\bar{S}_{\mathrm{A}}$, $\bar{S}_{\mathrm{B}}$, S_{A}, and S_{B}, are expressed by

$$\bar{S}_{\mathrm{A}} = \Phi_{\mathrm{A}_1}/(1 - K_{\mathrm{A}}\Phi_{\mathrm{A}_1})^2 \qquad (19)$$

$$\bar{S}_{\mathrm{B}} = \Phi_{\mathrm{B}_1}/(1 - K_{\mathrm{B}}\Phi_{\mathrm{B}_1})^2 \qquad (20)$$

$$S_{\mathrm{A}} = \Phi_{\mathrm{A}_1}/(1 - K_{\mathrm{A}}\Phi_{\mathrm{A}_1}) \qquad (21)$$

$$S_{\mathrm{B}} = \Phi_{\mathrm{B}_1}/(1 - K_{\mathrm{B}}\Phi_{\mathrm{B}_1}) \qquad (22)$$

The true molar volume of the quaternary mixture V is described as

$$\begin{aligned}\frac{1}{V} = {} & \frac{S_{\mathrm{A}}}{r_{\mathrm{A}}} + \frac{S_{\mathrm{B}}}{r_{\mathrm{B}}} + \left(\frac{2}{r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}} + \frac{S_{\mathrm{A}}}{r_{\mathrm{A}}} + \frac{S_{\mathrm{B}}}{r_{\mathrm{B}}}\right)\frac{r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}}{(1 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}})} \\ & + \frac{\Phi_{\mathrm{C}_1}}{r_{\mathrm{C}}}\Bigg\{1 + r_{\mathrm{C}}K_{\mathrm{AC}}S_{\mathrm{A}} + r_{\mathrm{C}}K_{\mathrm{BC}}S_{\mathrm{B}} \\ & + \left[\left(\frac{1}{r_{\mathrm{B}}K_{\mathrm{AB}}} + S_{\mathrm{A}}\right)K_{\mathrm{AC}} + \left(\frac{1}{r_{\mathrm{A}}K_{\mathrm{AB}}} + S_{\mathrm{B}}\right)K_{\mathrm{BC}}\right]\frac{r_{\mathrm{A}}r_{\mathrm{B}}r_{\mathrm{C}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}}{(1 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}})}\Bigg\} \\ & + \frac{\Phi_{\mathrm{D}_1}}{r_{\mathrm{D}}}\Bigg\{1 + r_{\mathrm{D}}K_{\mathrm{AD}}S_{\mathrm{A}} + r_{\mathrm{D}}K_{\mathrm{BD}}S_{\mathrm{B}} \\ & + \left[\left(\frac{1}{r_{\mathrm{B}}K_{\mathrm{AB}}} + S_{\mathrm{A}}\right)K_{\mathrm{AD}} + \left(\frac{1}{r_{\mathrm{A}}K_{\mathrm{AB}}} + S_{\mathrm{B}}\right)K_{\mathrm{BD}}\right]\frac{r_{\mathrm{A}}r_{\mathrm{B}}r_{\mathrm{D}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}}{(1 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}})}\Bigg\}\end{aligned} \qquad (23)$$

The molecular structural parameters of the pure components, r and q, were calculated using the method of Vera et al. [19]. The association constants for alcohols at 50°C are 87.0 for 1-propanol and 23.1 for *tert*-butanol [20]. The molar enthalpy of the hydrogen bond for alcohols was taken as $-23.2\ \mathrm{kJ\ mol^{-1}}$ [21]. The solvation constants at 50°C and the enthalpies of complex formation were mainly taken from previous papers [6, 22, 23]: $K_{AB} = 25$ and $h_{AB} = -23.2\ \mathrm{kJ\ mol^{-1}}$ for 1-propanol + *tert*-butanol (this work); $K_{AC} = 30$ and $h_{AC} = -17\ \mathrm{kJ\ mol^{-1}}$ for 1-propanol + acetonitrile [22]; $K_{AD} = 2.5$ and $h_{AD} = -8.3\ \mathrm{kJ\ mol^{-1}}$ for 1-propanol + benzene [6]; $K_{BC} = 15$ and $h_{BC} = -17\ \mathrm{kJ\ mol^{-1}}$ for *tert*-butanol + acetonitrile [23]; $K_{BD} = 2.5$ and $h_{BD} = -8.3\ \mathrm{kJ\ mol^{-1}}$ for *tert*-butanol + benzene [23]. All the h values were assumed to be temperature-independent and to fix the temperature dependence of the equilibrium constants via the van't Hoff relation. Table 2 shows the vapour pressures, liquid molar volumes, second virial coefficients and structural parameters for the pure components and the cross second virial coefficients used in data reduction.

The binary energy parameter of the model were sought using a computer program which minimizes the following objective function [24]

$$F = \sum_{i=1}^{N} \left[\frac{(P_i - P_i^*)^2}{\sigma_P^2} + \frac{(T_i - T_i^*)^2}{\sigma_T^2} + \frac{(x_{1i} - x_{1i}^*)^2}{\sigma_x^2} + \frac{(y_{1i} - y_{1i}^*)^2}{\sigma_y^2} \right] \tag{24}$$

where an asterisk represents the most probable calculated value and the standard deviations of the measured variables were set as $\sigma_P = 1$ Torr, $\sigma_T = 0.05$ K, $\sigma_x = 0.001$, and $\sigma_y = 0.003$. Table 3 shows the binary calculated results. Table 4

Table 2

Vapour pressures P_i^s, liquid molar volumes V_i^L, second virial coefficients B_{ii} and molecular structural parameters, r and q, for the pure components and cross second virial coefficients B_{ij} at 60°C

Pure component	1-Propanol	*tert*-Butanol	Acetonitrile	Benzene
P_i^s/Torr	152.7	289.8	368.0	391.5
$v_i^L/\mathrm{cm^3\ mol^{-1}}$	74.7	100.2	55.6	93.3
$-B_{ii}/\mathrm{cm^3\ mol^{-1}}$	1493	1397	3475	1110
r	2.23	2.77	1.50	2.56
q	1.98	2.42	1.40	2.05

Mixture	$-B_{ij}/\mathrm{cm^3\ mol^{-1}}$	Mixture	$-B_{ij}/\mathrm{cm^3\ mol^{-1}}$
1-Propanol + *tert*-butanol	1781	*tert*-Butanol + acetonitrile	2017
1-Propanol + acetonitrile	1909	*tert*-Butanol + benzene	893
1-Propanol + benzene	786	Acetonitrile + benzene	1057

Table 3

Binary calculated results

System (A + B)	Temp./°C	Number of data points	Root-mean-square deviations				Parameters	
			δP/Torr	δT/K	$\delta x \times 10^3$	$\delta y \times 10^3$	a_{AB}/K	a_{BA}/K
Acetonitrile + benzene	45	12	0.78	0.02	0.5	3.6	−10.54	258.38
tert-Butanol + acetonitrile	60	11	2.06	0.00	0.9	5.9	523.91	82.74
tert-Butanol + benzene	45	11	1.17	0.00	0.7	4.7	133.89	31.33
1-Propanol + acetonitrile	55	9	1.51	0.00	0.8	4.1	580.27	49.41
1-Propanol + benzene	45	11	0.14	0.00	0.1	1.4	114.53	−8.23
1-Propanol + *tert*-butanol	40	15	0.14	0.00	1.2		−31.38	92.88

Table 4
Prediction of isothermal quaternary vapour–liquid equilibria

System	Temp./°C	Number of data points	Dev. [a]	Vapour mole fractions				Pressure		Ref.
				$\delta y_1 \times 10^3$	$\delta y_2 \times 10^3$	$\delta y_3 \times 10^3$	$\delta y_4 \times 10^3$	δP/Torr	$(\delta P/P)$/%	
Methanol(1) + ethanol(2)			I	5.5	7.4	3.6	7.1	2.34	0.71	
+ acetonitrile(3) + benzene(4)	45	25	II	6.5	9.1	4.8	9.5	3.02	0.93	1
Ethanol(1) + 1-propanol(2)			I	2.1	3.4	6.0	3.8	2.30	1.01	
+ acetonitrile(3) + benzene(4)	45	24	II	2.7	4.4	6.7	4.8	2.91	1.20	2
Methanol(1) + 1-propanol(2)			I	5.0	3.3	7.5	6.0	3.22	0.72	
+ acetonitrile(3) + benzene(4)	55	24	II	6.6	4.1	8.9	7.3	3.86	0.86	3
Methanol(1) + 1-butanol(2)			I	7.4	4.4	5.6	7.8	3.31	0.79	
+ acetonitrile(3) + benzene(4)	55	26	II	9.7	4.6	7.0	9.6	3.91	0.97	4
Methanol(1) + 2-propanol(2)			I	4.0	2.6	3.1	7.5	2.03	0.41	
+ acetonitrile(3) + benzene(4)	55	21	II	5.6	3.5	4.1	8.9	2.44	0.50	5
Methanol(1) + isobutanol(2)			I	7.2	6.6	4.2	5.9	3.97	0.71	
+ acetonitrile(3) + benzene(4)	60	13	II	9.1	6.6	5.1	7.9	4.52	0.82	6
Methanol(1) + *tert*-butanol(2)			I	6.6	7.3	5.9	7.6	3.42	0.63	
+ acetonitrile(3) + benzene(4)	60	14	II	7.7	8.0	6.7	8.5	3.95	0.73	6
1-Propanol(1) + *tert*-butanol(2)			I	2.0	4.5	9.0	5.4	3.00	0.67	
+ acetonitrile(3) + benzene(4)	60	23	II	2.5	5.2	10.3	6.2	3.54	0.80	This work

[a] I, absolute arithmetic mean deviation; II, root-mean-squared deviation.

gives the deviations between the experimental and predicted values of the quaternary VLE, together with those for seven other systems [1–6], indicating that agreement is good.

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References

[1] I. Nagata, Thermochim. Acta, 157 (1990) 95–104.
[2] I. Nagata, Phys. Chem. Liq., 21 (1990) 137–145.
[3] I. Nagata, J. Chem. Thermodyn., 22 (1990) 501–504.
[4] I. Nagata, J. Chem. Thermodyn., 23 (1991) 293–296.
[5] I. Nagata, Y. Fukushima and K. Miyazaki, Fluid Phase Equilibria, 71 (1992) 17–27.
[6] I. Nagata, Thermochim. Acta, 214 (1993) 349–359.
[7] I. Nagata, Fluid Phase Equilibria, 19 (1985) 153–174.
[8] I. Nagata and K. Ohtsubo, Thermochim. Acta, 102 (1986) 185–205.
[9] P. Oracz, Int. Data Ser. A, 17 (1989) 292.
[10] T. Ohta, T. Kinoshita and I. Nagata, J. Chem. Eng. Data, 28 (1983) 36–39.
[11] I. Brown and F. Smith, Aust. J. Chem., 12 (1959) 407–412.
[12] I. Nagata, Thermochim. Acta, 126 (1988) 107–116.
[13] I. Brown, W. Fock and F. Smith, J. Chem. Thermodyn., 1 (1969) 273–291.
[14] I. Brown and F. Smith, Aust. J. Chem., 8 (1955) 62–67.
[15] J.A. Riddick, W.B. Bunger and T.K. Sakano, Organic Solvents, 4th edn., Wiley-Interscience, New York, 1986.
[16] I. Nagata, J. Chem. Eng. Data, 30 (1985) 201–203.
[17] C.F. Spencer and R.P. Danner, J. Chem. Eng. Data, 17 (1972) 236–241.
[18] J.G. Hayden and J.P. O'Connell, Ind. Eng. Chem. Proc. Des. Dev., 14 (1975) 209–216.
[19] J.H. Vera, S.G. Sayegh and G.A. Ratcliff, Fluid Phase Equilibria, 1 (1977) 113–135.
[20] V. Brandani, Fluid Phase Equilibria, 12 (1983) 87–104.
[21] R.H. Stokes and C. Burfitt, J. Chem. Thermodyn., 5 (1973) 623–631.
[22] I. Nagata, Fluid Phase Equilibria, 24 (1985) 279–287.
[23] I. Nagata, J. Chem. Thermodyn., 21 (1989) 225–229.
[24] J.M. Prausnitz, T.F. Anderson, E.A. Grens, C.A. Eckert, R. Hsieh, and J.P. O'Connell, Computer Calculations for Multicomponent Vapor–Liquid and Liquid–Liquid Equilibria, Prentice-Hall, Englewood Cliffs, NJ, 1980, Chapters 3, 4, 6, and Appendices C and D.