Thermochimica Acta, 214 (1993) 349–359
Elsevier Science Publishers B.V., Amsterdam

Isothermal vapour–liquid equilibrium for two quaternary systems including two alcohols, acetonitrile and benzene

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(Received 24 April 1992)

Abstract

Vapour–liquid equilibrium data have been reported for the quaternary systems methanol + isobutanol + acetonitrile + benzene, and methanol + *tert*-butanol + acetonitrile + benzene at 60°C using a modified Boublik vapour-recirculating still. The experimental results agree well with those calculated by the UNIQUAC associated-solution model with binary parameters alone.

LIST OF SYMBOLS

a_{IJ}	binary interaction energy parameter for the I–J pair
A, B, C, D	methanol, isobutanol or *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 the I–J pair
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 eqn. (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

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$P_{\mathrm{I}}^{\mathrm{s}}$	saturated vapour pressure of pure component I
q_{I}	molecular geometric-area parameter, pure component I
R	universal gas constant
r_{I}	molecular geometric-size parameter, pure component I
$\bar{S}_{\mathrm{A}}, \bar{S}_{\mathrm{B}}$	sums as defined by eqns. (19) and (20)
$S_{\mathrm{A}}, S_{\mathrm{B}}$	sums as defined by eqns. (21) and (22)
T	absolute temperature
$v_{\mathrm{I}}^{\mathrm{L}}$	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

Greek letters

γ_{I}	activity coefficient of component I
θ_{I}	area fraction of component I
$\sigma_P, \sigma_T, \sigma_x, \sigma_y$	standard deviations in pressure, temperature, liquid-phase mole fraction and vapour-phase mole fraction
τ_{IJ}	$\exp(-a_{\mathrm{IJ}}/T)$
ϕ_{I}	fugacity coefficient of component I at P and T
$\phi_{\mathrm{I}}^{\mathrm{s}}$	fugacity coefficient of pure component I at $P_{\mathrm{I}}^{\mathrm{s}}$ and T
Φ_{I}	segment fraction of component I
Φ_{I1}	monomer segment fraction of component I
Φ_{I1}^{0}	monomer segment fractions of pure alcohol I

Subscripts

A, B, C, D	alcohols and active non-associating components
$\mathrm{A}_1, \mathrm{B}_1, \mathrm{C}_1, \mathrm{D}_1$	monomers of components A, B, C and D
$\mathrm{A}_i, \mathrm{B}_i$	*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

Superscript

*	reference state of 50°C or calculated value

INTRODUCTION

In continuing studies on quaternary vapour–liquid equilibrium (VLE) measurements [1–5], this paper reports experimental data for the methanol + isobutanol or *tert*-butanol + acetonitrile + benzene systems at 60°C and the experimental results are compared with those predicted from the UNIQUAC associated-solution model with only binary parameters [1, 6, 7]. The following binary VLE data were used to obtain the binary energy parameters of the model: methanol + isobutanol or *tert*-butanol at 25°C [8]; methanol + acetonitrile at 55°C [9]; methanol + benzene at 55°C [10]; isobutanol + acetonitrile at 60°C [11]; isobutanol + benzene at 45°C [12]; *tert*-butanol + acetonitrile at 60°C [13]; *tert*-butanol + benzene at 45°C [12]; acetonitrile + benzene at 45°C [14].

EXPERIMENTAL

Isobutanol (2-methyl-1-propanol), *tert*-butanol (2-methyl-2-propanol) and acetonitrile (Wako Pure Chemical Industries Ltd., guaranteed reagent grade) were used without further purification. Methanol (first grade) was shaken with calcium oxide and distilled fractionally in 1 m glass columns with McMahon packing. Benzene (first grade) was subjected to repeated recrystallization. Densities of the compounds used for experimental work were measured with an Anton Paar densimeter DMA 40 at 25 or 30°C and agreed well with literature values [15]. A modified Boublik vapour-recirculating still was used to obtain VLE data as described previously [16]. Compositions of equilibrated liquid- and vapour-phase samples were analysed using a Shimadzu gas chromatograph GC-7A and a Shimadzu Chromatopac E-1B. The 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.

The experimental VLE data are given in Table 1, together with the activity coefficients γ_I and the fugacity coefficients ϕ_I derived from eqns. (1) and (2) below

$$\gamma_I = P\phi_I y_I / \{x_I P_I^s \phi_I^s \exp[v_I^L(P - P_I^s)/RT]\} \qquad (1)$$

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

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, and T the absolute temperature; v^L the pure-liquid molar volume was estimated from a modified Rackett equation [17] and the second virial coefficients B were estimated using the correlation of Hayden and O'Connell [18].

TABLE 1

Quaternary experimental vapour–liquid equilibrium data for two systems 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
	Methanol (1) + isobutanol (2) + acetonitrile (3) + benzene (4)																
1	0.497	0.113	0.056	0.334	0.563	0.021	0.049	0.367	723.1	1.303	1.374	1.694	2.034	0.963	0.944	0.927	0.938
2	0.155	0.176	0.173	0.496	0.302	0.049	0.172	0.477	574.8	1.808	1.660	1.547	1.413	0.977	0.957	0.937	0.981
3	0.082	0.156	0.162	0.600	0.205	0.058	0.179	0.558	532.6	2.161	2.066	1.604	1.265	0.982	0.962	0.944	0.980
4	0.067	0.301	0.510	0.122	0.145	0.108	0.540	0.207	423.8	1.493	1.600	1.216	1.877	0.985	0.969	0.938	1.001
5	0.055	0.140	0.626	0.179	0.128	0.059	0.547	0.266	473.3	1.792	2.095	1.113	1.831	0.985	0.968	0.931	0.999
6	0.313	0.267	0.054	0.366	0.448	0.051	0.064	0.437	598.4	1.376	1.182	1.925	1.828	0.973	0.953	0.940	0.982
7	0.200	0.321	0.262	0.217	0.327	0.077	0.284	0.312	512.8	1.353	1.280	1.502	1.905	0.976	0.959	0.935	0.991
8	0.055	0.140	0.626	0.179	0.128	0.059	0.547	0.266	473.3	1.792	2.095	1.113	1.831	0.985	0.968	0.931	0.999
9	0.395	0.137	0.133	0.335	0.488	0.027	0.121	0.364	689.7	1.360	1.394	1.676	1.920	0.966	0.946	0.925	0.984
10	0.272	0.128	0.352	0.248	0.393	0.032	0.283	0.292	632.0	1.463	1.629	1.351	1.920	0.970	0.951	0.920	0.990
11	0.619	0.161	0.061	0.159	0.634	0.027	0.074	0.265	670.8	1.093	1.154	2.182	2.885	0.963	0.946	0.929	0.991
12	0.138	0.130	0.365	0.367	0.270	0.040	0.309	0.381	577.4	1.822	1.843	1.310	1.542	0.976	0.957	0.928	0.987
13	0.127	0.133	0.195	0.545	0.289	0.041	0.188	0.482	581.8	2.137	1.861	1.516	1.315	0.977	0.957	0.936	0.981
	Methanol (1) + *tert*-butanol (2) + acetonitrile (3) + benzene (4)																
1	0.591	0.168	0.073	0.168	0.591	0.061	0.075	0.273	691.0	1.098	0.834	1.899	2.894	0.962	0.947	0.926	0.989
2	0.063	0.131	0.628	0.178	0.134	0.126	0.490	0.241	522.7	1.802	1.708	1.110	1.841	0.981	0.967	0.925	0.998
3	0.067	0.252	0.499	0.182	0.118	0.207	0.431	0.244	515.8	1.470	1.440	1.194	1.794	0.979	0.967	0.928	0.995
4	0.110	0.370	0.355	0.165	0.156	0.261	0.352	0.231	515.9	1.181	1.235	1.375	1.871	0.977	0.966	0.930	0.994
5	0.067	0.269	0.537	0.127	0.114	0.229	0.471	0.186	505.3	1.392	1.464	1.187	1.927	0.980	0.968	0.927	0.999
6	0.065	0.404	0.131	0.400	0.105	0.282	0.159	0.454	519.0	1.357	1.231	1.715	1.507	0.980	0.967	0.943	0.982
7	0.111	0.399	0.119	0.371	0.164	0.260	0.145	0.431	527.1	1.258	1.165	1.747	1.568	0.978	0.965	0.942	0.982
8	0.123	0.650	0.064	0.163	0.161	0.433	0.114	0.292	452.3	0.956	1.027	2.206	2.087	0.977	0.969	0.948	0.988
9	0.119	0.358	0.359	0.164	0.171	0.247	0.349	0.233	521.7	1.209	1.221	1.362	1.920	0.976	0.965	0.930	0.994
10	0.064	0.114	0.644	0.178	0.142	0.111	0.504	0.243	522.6	1.880	1.729	1.093	1.856	0.981	0.967	0.925	0.998
11	0.050	0.254	0.529	0.167	0.089	0.221	0.460	0.230	503.2	1.451	1.490	1.171	1.801	0.980	0.968	0.928	0.997
12	0.269	0.095	0.180	0.456	0.416	0.048	0.145	0.391	695.7	1.719	1.171	1.494	1.525	0.967	0.948	0.923	0.982
13	0.113	0.500	0.232	0.155	0.149	0.333	0.278	0.240	496.3	1.055	1.123	1.607	1.987	0.976	0.967	0.935	0.992
14	0.380	0.127	0.126	0.367	0.467	0.058	0.112	0.363	708.9	1.389	1.077	1.680	1.795	0.965	0.947	0.924	0.983

DATA ANALYSIS

The experimental results were analysed using the UNIQUAC associated-solution model. We assume that in a quaternary mixture including two alcohols (A and B), acetonitrile (C) and benzene (D), many chemical complexes are formed according to the association and multi-solvation of alcohol molecules and the solvation between the terminal hydroxy groups of alcohol polymers and copolymers and acetonitrile or benzene. Their general formulae are A_i, B_i, $(A_iB_j)_k$, $(B_iA_j)_k$, $A_i(B_jA_k)_l$, $B_i(A_jB_k)_l$, 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 $B_i(A_jB_k)_lD$. The equilibrium constants for chemical-complex-forming reactions are assumed to be independent of the degrees of homo-association and hetero-association and are defined as

$$\begin{aligned} K_A &= \frac{\Phi_{A_{i+1}}}{\Phi_{A_i}\Phi_{A_1}}\frac{i}{i+1} \qquad \text{for} \quad A_i + A_1 = A_{i+1} \\ &= K_A^* \exp\left[-\frac{h_A}{R}\left(\frac{1}{T}-\frac{1}{T^*}\right)\right] \end{aligned} \tag{3}$$

$$\begin{aligned} K_B &= \frac{\Phi_{B_{i+1}}}{\Phi_{B_i}\Phi_{B_1}}\frac{i}{i+1} \qquad \text{for} \quad B_i + B_1 = B_{i+1} \\ &= K_B^* \exp\left[-\frac{h_B}{R}\left(\frac{1}{T}-\frac{1}{T^*}\right)\right] \end{aligned} \tag{4}$$

$$\begin{aligned} K_{AB} &= \frac{\Phi_{A_iB_jA_kB_l}}{\Phi_{A_iB_jA_k}\Phi_{B_l}}\frac{r_{A_iB_jA_k}r_{B_l}}{r_{A_iB_jA_kB_l}r_Ar_B} \qquad \text{for} \quad A_iB_jA_k + B_l = A_iB_jA_kB_l \\ &= K_{AB}^* \exp\left[-\frac{h_{AB}}{R}\left(\frac{1}{T}-\frac{1}{T^*}\right)\right] \end{aligned} \tag{5}$$

$$\begin{aligned} K_{AC} &= \frac{\Phi_{A_iC}}{\Phi_{A_i}\Phi_{C_1}}\frac{1}{ir_A + r_C} \qquad \text{for} \quad A_i + C_1 = A_iC \\ &= K_{AC}^* \exp\left[-\frac{h_{AC}}{R}\left(\frac{1}{T}-\frac{1}{T^*}\right)\right] \end{aligned} \tag{6}$$

$$\begin{aligned} K_{BC} &= \frac{\Phi_{B_iC}}{\Phi_{B_i}\Phi_{C_1}}\frac{1}{ir_B + r_C} \qquad \text{for} \quad B_i + C_1 = B_iC \\ &= K_{BC}^* \exp\left[-\frac{h_{BC}}{R}\left(\frac{1}{T}-\frac{1}{T^*}\right)\right] \end{aligned} \tag{7}$$

K_{AD} and K_{BD} are defined similarly as in eqns. (6) and (7), respectively.

The activity coefficients of methanol (A) and acetonitrile (C) are expressed by

$$\ln \gamma_A = \ln\left(\frac{\Phi_{A_1}}{\Phi^0_{A_1} X_A}\right) + \frac{r_A}{V^0_A} - \frac{r_A}{V} - \left(\frac{Z}{2}\right) q_A \left(\ln \frac{\Phi_A}{\theta_A} + 1 - \frac{\Phi_A}{\theta_A}\right)$$
$$+ q_A\left[1 - \ln\left(\sum_J \theta_A \tau_{JA}\right) - \sum_J \frac{\theta_J \tau_{AJ}}{\sum_K \theta_K \tau_{KJ}}\right] \quad (8)$$

$$\ln \gamma_C = \ln \frac{\Phi_{C_1}}{x_C} + 1 - \frac{r_C}{V} - \left(\frac{Z}{2}\right) q_C \left(\ln \frac{\Phi_C}{\theta_C} + 1 - \frac{\Phi_C}{\theta_C}\right)$$
$$+ q_C\left[1 - \ln\left(\sum_J \theta_C \tau_{JC}\right) - \sum_J \frac{\theta_J \tau_{CJ}}{\sum_K \theta_K \tau_{KJ}}\right] \quad (9)$$

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 Φ^0_{I1} and the true molar volume V^0_I for pure alcohol I are given by

$$\Phi_I = x_I r_I \Big/ \sum_J x_J r_J \quad (10)$$

$$\theta_I = x_I q_I \Big/ \sum_J x_J q_J \quad (11)$$

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

$$\Phi^0_{I1} = [2K_I + 1 - (1 + 4K_I)^{0.5}/2K_I^2 \quad (13)$$

$$V^0_I = r_I/(1 - K_I \Phi^0_{I1}) \quad (14)$$

The activity coefficients of the butanols (B) and benzene (D) are easily derived by changing the subscript A to B in eqn. (3) and C to D in eqn. (4). 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 eqns. (15)–(18):

$$\Phi_A = (1 + r_A K_{AC} \Phi_{C_1} + r_A K_{AD} \Phi_{D_1}) \bar{S}_A + \frac{r_A K_{AB} \bar{S}_A S_B}{(1 - r_A r_B K^2_{AB} S_A S_B)^2}$$
$$\times \{2 + r_B K_{AB} S_A (2 - r_A r_B K^2_{AB} S_A S_B) + r_A K_{AB} S_B$$
$$+ \Phi_{C_1}[(r_A K_{AC} + r_B K_{BC}) + r_A r_B K_{AB} K_{AC} S_A (2 - r_A r_B K^2_{AB} S_A S_B)$$
$$+ r_A r_B K_{AB} K_{BC} S_B]$$
$$+ \Phi_{D_1}[(r_A K_{AD} + r_B K_{BD})$$
$$+ r_A r_B K_{AB} K_{AD} S_A (2 - r_A r_B K^2_{AB} S_A S_B)$$
$$+ r_A r_B K_{AB} K_{BD} S_B]\} \quad (15)$$

$$\begin{aligned}\Phi_B = {} & (1 + r_B K_{BC}\Phi_{C_1} + r_B K_{BD}\Phi_{D_1})\bar{S}_B + \frac{r_B K_{AB} S_A \bar{S}_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)^2} \\ & \times \{2 + r_A K_{AB} S_B(2 - r_A r_B K_{AB}^2 S_A S_B) + r_B K_{AB} S_A \\ & + \Phi_{C_1}[(r_A K_{AC} + r_B K_{BC}) + r_A r_B K_{AB} K_{BC} S_B(2 - r_A r_B K_{AB}^2 S_A S_B) \\ & + r_A r_B K_{AB} K_{AC} S_A] \\ & + \Phi_{D_1}[(r_A K_{AD} + r_B K_{BD}) + r_A r_B K_{AB} K_{BD} S_B(2 - r_A r_B K_{AB}^2 S_A S_B) \\ & + r_A r_B K_{AB} K_{AD} S_A]\} \end{aligned} \qquad (16)$$

$$\begin{aligned}\Phi_C = {} & \Phi_{C_1}\left\{1 + r_C K_{AC} S_A + r_C K_{BC} S_B + \frac{r_A r_B r_C K_{AB}^2 S_A S_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)}\right. \\ & \left.\times \left[\frac{K_{AC}}{r_B K_{AB}} + \frac{K_{BC}}{r_A K_{AB}} + K_{AC} S_A + K_{BC} S_B\right]\right\} \end{aligned} \qquad (17)$$

$$\begin{aligned}\Phi_D = {} & \Phi_{D_1}\left\{1 + r_D K_{AD} S_A + r_D K_{BD} S_B + \frac{r_A r_B r_D K_{AB}^2 S_A S_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)}\right. \\ & \left.\times \left[\frac{K_{AD}}{r_B K_{AB}} + \frac{K_{BD}}{r_A K_{AB}} + K_{AD} S_A + K_{BD} S_B\right]\right\} \end{aligned} \qquad (18)$$

where the sums $\bar{S}_A$, $\bar{S}_B$, S_A and S_B, are written

$$\bar{S}_A = \Phi_{A_1}/(1 - K_A \Phi_{A_1})^2 \qquad (19)$$

$$\bar{S}_B = \Phi_{B_1}/(1 - K_B \Phi_{B_1})^2 \qquad (20)$$

$$S_A = \Phi_{A_1}/(1 - K_A \Phi_{A_1}) \qquad (21)$$

$$S_B = \Phi_{B_1}/(1 - K_B \Phi_{B_1}) \qquad (22)$$

The true molar volume of the mixture V is described as

$$\begin{aligned}\frac{1}{V} = {} & \frac{S_A}{r_A} + \frac{S_B}{r_B} + \left(\frac{2}{r_A r_B K_{AB}} + \frac{S_A}{r_A} + \frac{S_B}{r_B}\right)\frac{r_A r_B K_{AB}^2 S_A S_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)} \\ & + \frac{\Phi_{C_1}}{r_C}\left\{1 + r_C K_{AC} S_A + r_C K_{BC} S_B\right. \\ & \left. + \left[\left(\frac{1}{r_B K_{AB}} + S_A\right)K_{AC} + \left(\frac{1}{r_A K_{AB}} + S_B\right)K_{BC}\right]\frac{r_A r_B r_C K_{AB}^2 S_A S_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)}\right\} \\ & + \frac{\Phi_{D_1}}{r_D}\left\{1 + r_D K_{AD} S_A + r_D K_{BD} S_B\right. \\ & \left. + \left[\left(\frac{1}{r_B K_{AB}} + S_A\right)K_{AD} + \left(\frac{1}{r_A K_{AB}} + S_B\right)K_{BD}\right]\frac{r_A r_B r_D K_{AB}^2 S_A S_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)}\right\} \end{aligned} \qquad (23)$$

The molecular structural parametes 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: 173.9 for methanol; 50.6 for isobutanol;

and 23.1 for *tert*-butanol [20]. The molar enthalpy of the hydrogen bond for alcohols was taken as -23.2 kJ mol^{-1} [21]. The solvation constants at 50°C and enthalpies of complex formation taken from previous papers [6, 22–24] are: $K_{AB} = 80$ and $h_{AB} = -23.2$ kJ mol^{-1} for methanol + isobutanol; $K_{AC} = 30$ and $h_{AC} = -17$ kJ mol^{-1} for methanol + acetonitrile; $K_{AD} = 4$ and $h_{AD} = -8.3$ kJ mol^{-1} for methanol + benzene; $K_{BC} = 30$ and $h_{BC} = -17$ kJ mol^{-1} for isobutanol + acetonitrile; $K_{BD} = 2$ and $h_{BD} = -8.3$ kJ mol^{-1} for isobutanol + benzene; $K_{AB} = 55$ and $h_{AB} = -23.2$ kJ mol^{-1} for methanol + *tert*-butanol; $K_{BC} = 15$ and $h_{BC} = -17$ kJ mol^{-1} for *tert*-butanol + acetonitrile; $K_{BD} = 2.5$ and $h_{BD} = -8.3$ kJ mol^{-1} for *tert*-butanol + benzene. All the h values were assumed to be temperature independent and to fix the temperature dependence of the equilibrium constants through the van't Hoff relation. Table 2 gives 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 analysis.

The binary energy parameters of the model were determined as described by Prausnitz et al. [25] using a computer program which minimizes the objective function

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

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

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 section virial coefficients B_{ij} at 60°C

	Methanol	Isobutanol	*tert*-Butanol	Acetonitrile	Benzene
P_i^s (Torr)	629.8	93.0	289.8	368.0	391.5
v_i^L (cm^3 mol^{-1})	41.3	97.7	100.2	55.6	93.3
B_{ii} (cm^3 mol^{-1})	−1305	−2455	−1397	−3475	−1110
r	1.15	2.77	2.77	1.50	2.56
q	1.12	2.42	2.42	1.40	2.05

Mixture	B_{ij} (cm^3 mol^{-1})	Mixture	B_{ij} (cm^3 mol^{-1})
Methanol + isobutanol	−1453	Acetonitrile + benzene	−1057
Methanol + acetonitrile	−1691	Methanol + *tert*-butanol	−1463
Methanol + benzene	−420	*tert*-Butanol + acetonitrile	−2017
Isobutanol + acetonitrile	−2007	*tert*-Butanol + benzene	−893
Isobutanol + benzene	−907		

TABLE 3

Binary calculated results

System (A + B)	Temp. (°C)	Number of data points	Root-mean-square deviations				Parameters	
			δP (Torr)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)	a_{AB} (K)	a_{BA} (K)
Acetonitrile + benzene	45	12	0.78	0.02	0.5	3.6	−10.54	258.38
Isobutanol + acetonitrile	60	14	2.02	0.00	1.5	5.3	638.85	104.83
Isobutanol + benzene	45	10	0.08	0.00	0.3	2.4	−8.36	154.38
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
Methanol + acetonitrile	55	13	1.59	0.00	1.2	5.3	480.17	−113.15
Methanol + benzene	55	9	0.94	0.06	1.4	4.7	−71.04	220.25
Methanol + isobutanol	25	14	2.02	0.02	0.3	6.2	−44.94	258.17
Methanol + *tert*-butanol	25	19	0.56	0.01	0.2	1.6	−75.96	182.54

TABLE 4

Prediction of isothermal quaternary varpour–liquid equilibria

System	Temp. (°C)	Number of data points	Dev. [a]	Vapour mole fractions				Pressure		Ref.
				δy_1 ($\times 10^3$)	δy_2 ($\times 10^3$)	δy_3 ($\times 10^3$)	δy_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	This work
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	This work

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

calculated results. Table 4 shows the deviations between the experimental and predicted values of quaternary VLE together with those for other systems [1–5], indicating that agreement is good.

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