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ISOTHERMAL VAPOUR–LIQUID EQUILIBRIA FOR BINARY MIXTURES OF METHYLCYCLOHEXANE WITH ALCOHOLS

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ABSTRACT

Vapour–liquid equilibrium data at 60 °C are presented for systems of methylcyclohexane with 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol, and 1-propanol. Experimental results were obtained using a Boublik vapour-recirculating still, and are well correlated with two models: the extended UNIQUAC, and the UNIQUAC associated-solution model.

LIST OF SYMBOLS

A, B	components
a_{IJ}	binary interaction parameter related to τ_{IJ}
B_{IJ}	second virial coefficient
F	objective function as defined by eqn. (14)
K_A	alcohol association constant, $(\Phi_{A_{i+1}}/\Phi_{A_i}\Phi_{A_1})[i/(i+1)]$
P	total pressure
P_I^s	vapour pressure of pure component I
q_I	molecular geometric area parameter of pure component I
q_I'	molecular interaction area parameter of pure component I in the extended UNIQUAC model
R	universal gas constant
r_I	molecular geometric volume parameter of pure component I
T	absolute temperature
V	true molar volume of alcohol mixture
$V_A^{\ominus}$	true molar volume of pure alcohol solution
V_I^L	molar liquid volume of pure component I
y_I	vapour phase mole fraction of component I
Z	coordination number, here equal to 10

Greek letters

γ_I	activity coefficient of component I
θ_I	area fraction of component I

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σ_P, σ_T	standard deviations in pressure and temperature
σ_x, σ_y	standard deviations in liquidphase and vapour phase mole fractions
τ_{IJ}	binary parameter as defined by $\exp(-a_{IJ}/T)$
Φ_I	segment fraction of component I
Φ_{A_1}	monomer segment fraction of alcohol in mixture
$\Phi_{A_1}^{\ominus}$	monomer segment fraction of pure alcohol
ϕ_I	vapour-phase fugacity coefficient of component I
ϕ_I^s	vapour-phase fugacity coefficient of pure component I at P_I^s and T

Subscripts

A, B	components
A_1	monomer of alcohol
I, J	components

INTRODUCTION

The vapour–liquid equilibria for the systems of methylcyclohexane with 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol and 1-propanol have not previously been investigated [1]. The purpose of this work was to provide equilibrium data for these five binary systems at 60 ° C. This paper presents the experimental data for the systems and the correlated results derived from the extended UNIQUAC and UNIQUAC associated-solution models.

EXPERIMENTAL

Reagent grade methylcyclohexane and butanols (Wako Pure Chemical Industries Ltd.) were used directly. Reagent grade 1-propanol was fractionated after drying over calcium oxide. The density of each chemical at 25 ° C was measured with an Anton Paar densimeter (DMA40). Vapour pressures of the chemicals were measured at 60 ° C using a Boublik vapour-recirculating equilibrium still [2]. Densities and vapour pressures of the chemicals are shown in Table 1. All necessary corrections were added to observed pressures to give the corresponding height of a mercury column at 0 ° C and standard gravity.

The compositions of the vapour and liquid samples of the methylcyclohexane-2-methyl-1-propanol system were analysed with a Shimadzu gas chromatograph (GC-7A) and a Shimadzu integrator (Chromatopac E1A). Those of the other systems were obtained from measurements of their refractive indices at 25 ° C (30 ° C for 2-methyl-2-propanol-methylcyclohex-

TABLE 1

Densities and vapour pressures of pure components

Component	Density at 25 ° C (g mol^{-1})		Vapour pressure at 60 ° C (mmHg)	
	Obs.	Lit. (3)	Obs.	Lit. (3)
Methylcyclohexane	0.7651	0.7651	202.9	202.89
1-Butanol	0.8060	0.8060	59.0	59.01
2-Butanol	0.8026	0.8026	139.3	139.31
2-Methyl-1-propanol	0.7978	0.7978	93.0	93.01
2-Methyl-2-propanol	0.7757 [a]	0.7757	289.8	298.76
1-Propanol	0.7997	0.7998	152.3	152.26

[a] At 30 ° C.

ane) using a Shimadzu Pulfrich refractometer. Experimental error is taken to be: vapour and liquid mole fractions, ± 0.002; pressure, 0.16 mmHg; temperature, 0.05 ° C.

Table 2 gives the vapour–liquid equilibrium data for the five systems at 60 ° C. The activity coefficients γ and the fugacity coefficients ϕ were calculated from the following equations

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

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

where P, P_I^{s}, x_I and y_I are the measured values of total pressure, pure-component vapour pressure, liquid-phase and vapour-phase mole fractions respectively. v_I^{L} is the pure-liquid molar volume, estimated using a modified Rackett equation [4]; and B_{IJ} are the second virial coefficients, calculated from the correlation of Hayden and O'Connell [5].

DATA ANALYSIS

The experimental results were correlated using the extended UNIQUAC [6] and UNIQUAC associated-solution models [7]. These models give the following expressions for the activity coefficient.

Extended UNIQUAC model

$$\ln \gamma_A = \ln\frac{\Phi_A}{x_A} + 1 - \frac{\Phi_A}{x_A} - \left(\frac{Z}{2}\right)q_A\left(\ln\frac{\Phi_A}{\theta_A} + 1 - \frac{\Phi_A}{\theta_A}\right) - q_A' \ln(\theta_A + \theta_B\tau_{BA})$$
$$+ q_A\theta_B\left[\left(\frac{q_A'}{q_A}\right)\left(\frac{\tau_{BA}}{\theta_A + \theta_B\tau_{BA}} - 1\right) - \left(\frac{q_B'}{q_B}\right)\left(\frac{\tau_{AB}}{\theta_B + \theta_A\tau_{AB}} - 1\right)\right] \tag{3}$$

TABLE 2

Vapour–liquid equilibrium data for five binary systems at 60 ° C

x_1	y_1	P (mmHg)	γ_1	γ_2	ϕ_1	ϕ_2
Methylcyclohexane(1)–1-butanol(2)						
0.027	0.278	83.0	4.285	1.041	0.998	0.989
0.148	0.629	147.0	3.104	1.078	0.989	0.986
0.216	0.700	168.4	2.704	1.085	0.987	0.986
0.324	0.761	192.3	2.232	1.145	0.984	0.986
0.434	0.782	206.9	1.839	1.342	0.983	0.985
0.569	0.807	214.2	1.497	1.616	0.982	0.986
0.680	0.826	219.4	1.313	2.011	0.981	0.987
0.741	0.836	220.9	1.227	2.358	0.981	0.987
0.797	0.846	220.0	1.160	2.841	0.981	0.987
0.836	0.855	223.3	1.124	3.331	0.980	0.988
0.901	0.869	223.0	1.059	4.982	0.980	0.988
0.975	0.931	215.5	1.013	10.078	0.981	0.992
Methylcyclohexane(1)–2-butanol(2)						
0.030	0.152	160.3	4.060	1.004	0.995	0.984
0.121	0.377	201.7	3.119	1.022	0.988	0.981
0.223	0.477	227.2	2.402	1.092	0.985	0.981
0.294	0.524	236.0	2.076	1.137	0.983	0.981
0.433	0.588	251.2	1.679	1.304	0.981	0.981
0.508	0.620	253.4	1.522	1.399	0.980	0.982
0.679	0.675	260.4	1.272	1.887	0.979	0.983
0.751	0.703	258.4	1.188	2.208	0.979	0.984
0.863	0.747	253.9	1.079	3.365	0.979	0.986
0.955	0.839	234.4	1.012	6.043	0.979	0.989
Methylcyclohexane(1)–2-methyl-1-propanol(2)						
0.044	0.273	123.4	3.827	1.006	0.995	0.986
0.112	0.456	158.3	3.205	1.038	0.990	0.985
0.176	0.551	180.9	2.807	1.054	0.987	0.984
0.181	0.558	183.4	2.802	1.058	0.987	0.984
0.293	0.642	209.0	2.262	1.131	0.984	0.984
0.406	0.688	222.9	1.862	1.252	0.982	0.984
0.501	0.713	230.2	1.613	1.416	0.981	0.984
0.604	0.735	236.5	1.416	1.693	0.980	0.985
0.703	0.756	238.6	1.262	2.098	0.980	0.985
0.764	0.775	239.8	1.196	2.449	0.980	0.986
0.871	0.808	237.8	1.085	3.796	0.979	0.987
0.915	0.829	235.4	1.049	5.084	0.979	0.988
0.972	0.886	224.6	1.007	9.844	0.980	0.991
2-Methyl-2-propanol(1)–methylcyclohexane(2)						
0.015	0.130	228.3	6.916	0.992	0.993	0.980
0.071	0.299	279.5	4.092	1.033	0.988	0.976
0.163	0.402	314.3	2.685	1.098	0.985	0.974
0.213	0.435	322.9	2.282	1.133	0.984	0.974
0.269	0.465	330.0	1.972	1.180	0.983	0.974
0.357	0.506	338.5	1.656	1.270	0.982	0.974

TABLE 2 (continued)

x_1	y_1	P (mmHg)	γ_1	γ_2	ϕ_1	ϕ_2
2-Methyl-2-propanol(1)–methylcyclohexane(2)						
0.426	0.534	342.3	1.480	1.358	0.981	0.974
0.484	0.550	345.2	1.353	1.471	0.980	0.974
0.567	0.588	346.0	1.237	1.609	0.980	0.975
0.638	0.618	347.5	1.160	1.794	0.979	0.975
0.754	0.687	343.4	1.077	2.141	0.979	0.977
0.806	0.722	338.2	1.043	2.378	0.979	0.978
0.879	0.795	327.1	1.019	2.726	0.979	0.980
0.943	0.895	309.3	1.012	3.813	0.980	0.984
Methylcyclohexane(1)–1-propanol(2)						
0.092	0.351	218.4	4.126	1.022	0.986	0.986
0.174	0.465	250.1	3.295	1.060	0.982	0.986
0.261	0.531	269.4	2.694	1.118	0.980	0.986
0.375	0.585	282.7	2.164	1.228	0.978	0.986
0.421	0.588	284.1	1.946	1.323	0.978	0.986
0.499	0.606	286.9	1.708	1.477	0.977	0.987
0.588	0.624	288.3	1.499	1.723	0.977	0.987
0.620	0.629	289.5	1.439	1.851	0.977	0.987
0.702	0.639	288.7	1.288	2.291	0.977	0.987
0.828	0.672	285.8	1.136	3.573	0.976	0.988
0.896	0.705	276.6	1.067	5.151	0.977	0.989

$$\ln \gamma_B = \ln\frac{\Phi_B}{x_B} + 1 - \frac{\Phi_B}{x_B} - \left(\frac{Z}{2}\right) q_B\left(\ln\frac{\Phi_B}{\theta_B} + 1 - \frac{\Phi_B}{\theta_B}\right) - q'_B \ln(\theta_B + \theta_A\tau_{AB})$$

$$+ q_B\theta_A\left[\left(\frac{q'_B}{q_B}\right)\left(\frac{\tau_{AB}}{\theta_B + \theta_A\tau_{AB}} - 1\right) - \left(\frac{q'_A}{q_A}\right)\left(\frac{\tau_{BA}}{\theta_A + \theta_B\tau_{BA}} - 1\right)\right] \qquad (4)$$

where the segment fraction Φ_I, the surface fraction θ_I, and the binary parameter τ_{IJ} are given by

$$\Phi_I = \frac{r_I x_I}{\sum\limits_J r_J x_J} \qquad (5)$$

$$\theta_I = \frac{q_I x_I}{\sum\limits_J q_J x_J} \qquad (6)$$

$$\tau_{IJ} = \exp\left(-\frac{a_{IJ}}{T}\right) \qquad (7)$$

Z is the coordination number equal to 10, and r, q and q' are pure-component structural parameters (6, 8).

UNIQUAC associated-solution model

Subscripts A and B represent the alcohol and a saturated hydrocarbon respectively.

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

$$+ q_A\left[-\ln(\theta_A + \theta_B\tau_{BA}) + \theta_B\left(\frac{\tau_{BA}}{\theta_A + \theta_B\tau_{BA}} - \frac{\tau_{AB}}{\theta_B + \theta_A\tau_{AB}}\right)\right] \tag{8}$$

$$\ln \gamma_B = \ln\left(\frac{\Phi_{B_1}}{x_B}\right) + 1 - \frac{r_B}{V} - \left(\frac{Z}{2}\right) q_B\left(\ln\frac{\Phi_B}{\theta_B} + 1 - \frac{\Phi_B}{\theta_B}\right)$$

$$+ q_B\left[-\ln(\theta_B + \theta_A\tau_{AB}) + \theta_A\left(\frac{\tau_{AB}}{\theta_B + \theta_A\tau_{AB}} - \frac{\tau_{BA}}{\theta_A + \theta_B\tau_{BA}}\right)\right] \tag{9}$$

The monomer segment fraction of alcohol Φ_{A_1}, and the true molar volume of the mixture V are given by

$$\Phi_{A_1} = \frac{2K_A\Phi_A + 1 - \sqrt{1 + 4K_A\Phi_A}}{2K_A^2\Phi_A} \tag{10}$$

$$\frac{1}{V} = \frac{\Phi_{A_1}}{r_A\left(1 - K_A\Phi_{A_1}\right)} + \frac{\Phi_B}{r_B} \tag{11}$$

In the pure alcohol state Φ_{A_1} and V reduce to $\Phi_{A_1}^{\ominus}$ and $V_A^{\ominus}$, respectively.

$$\Phi_{A_1}^{\ominus} = \frac{2K_A + 1 - \sqrt{1 + 4K_A}}{2K_A^2} \tag{12}$$

$$\frac{1}{V_A^{\ominus}} = \frac{\left(1 - K_A\Phi_{A_1}^{\ominus}\right)}{r_A} \tag{13}$$

The association constants of the pure alcohols at 50 °C were taken from Brandani [9]: 87.0 for 1-propanol; 69.5 for 1-butanol; 31.1 for 2-butanol; 50.6 for 2-methyl-1-propanol; and 23.1 for 2-methyl-2-propanol. The enthalpy of hydrogen bond formation is -23.2 kJ mol^{-1} for all alcohols [10].

The values of r and q used in the UNIQUAC associated-solution model were estimated in accordance with the method of Vera et al. [11]. The values of the pure component structural parameters for the two models are given in Table 3.

The computer program used for parameter estimation was similar to that described by Prausnitz et al. [8]. A set of optimum parameters were obtained

TABLE 3

Pure component structural parameters for two models

Component	Extended UNIQUAC			UNIQUAC associated-solution	
	r	q	q'	r	q
Methylcyclohexane	4.64	3.55	$q^{0.2}$	3.72	2.98
1-Butanol	3.45	3.05	0.88	2.77	2.42
2-Butanol	3.45	3.05	0.88	2.77	2.42
2-Methyl-1-propanol	3.45	3.05	0.88	2.77	2.42
2-Methyl-2-propanol	3.45	3.05	0.88	2.77	2.42
1-Propanol	2.78	2.51	0.88	2.23	1.98

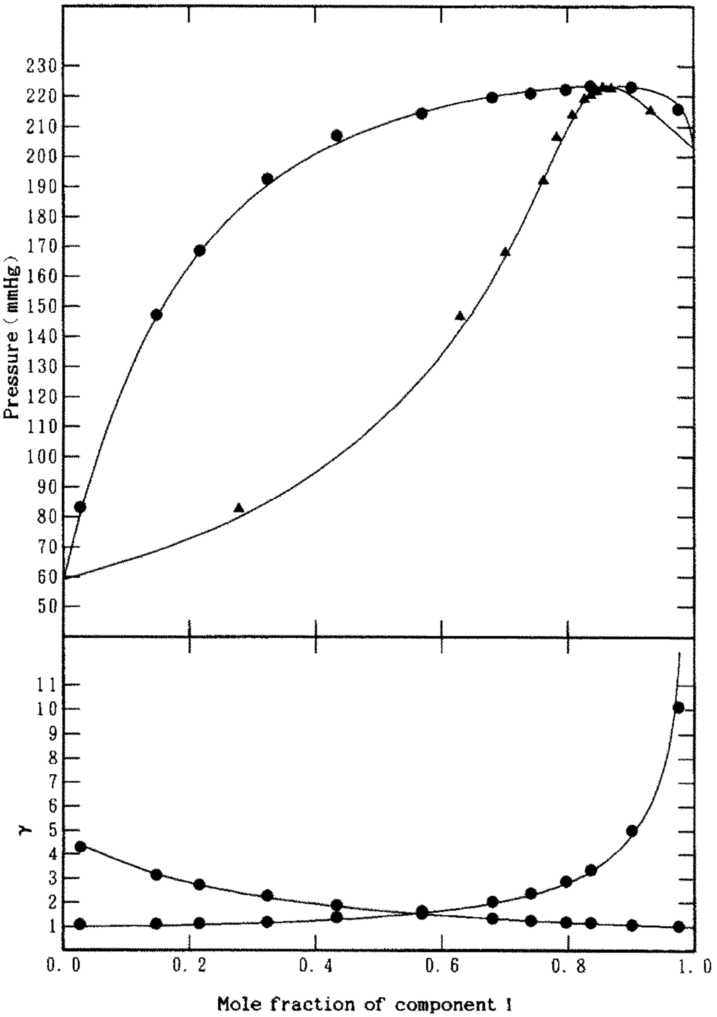

Fig. 1. Vapour–liquid equilibrium for methylcyclohexane(1)–1-butanol(2) at 60 °C. ▲, ●, Experimental; ———, calculated from the UNIQUAC associated-solution model.

TABLE 4

Binary calculated results of vapour–liquid equilibrium data reduction

System	Number of data points	Model [a]	Energy parameters		Root-mean-square deviations				Variance of fit [b]
			a_{AB} (K)	a_{BA} (K)	δP (mmHg)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)	
Methylcyclohexane (*A*)–	11	I	911.34	104.15	1.22	0.00	0.4	5.3	5.73
1-butanol (*B*)		II	−105.73	167.50	1.37	0.00	0.8	6.1	8.03
Methylcyclohexane (*A*)–	14	I	675.43	88.89	1.80	0.00	1.1	8.4	15.46
2-butanol (*B*)		II	−181.18	295.95	1.25	0.00	0.6	2.8	3.52
Methylcyclohexane (*A*)–	13	I	866.50	88.35	0.90	0.00	0.5	5.4	5.08
2-methyl-1-propanol (*B*)		II	−138.21	190.68	0.57	0.00	0.6	4.8	3.80
2-Methyl-2-propanol (*A*)–	14	I	53.58	621.18	1.18	0.00	0.7	5.3	5.82
methylcyclohexane (*B*)		II	242.10	−165.16	1.23	0.00	1.2	5.2	6.89
Methylcyclohexane (*A*)–	11	I	999.90	115.23	0.76	0.00	0.4	3.9	2.92
1-propanol (*B*)		II	−41.41	82.47	0.78	0.00	0.4	4.3	3.37

[a] I, extended UNIQUAC model; II, UNIQUAC associated-solution model.

[b] Variance of fit = (sum of squared, weighted residuals)/(number of degrees of freedom) = F/(number of data points − number of parameters).

by minimizing the objective function

$$F=\sum_{i}^{N}\left[\frac{(P_i-\hat{P}_i)^2}{\sigma_P^2}+\frac{(T_i-\hat{T}_i)^2}{\sigma_T^2}+\frac{(x_{1i}-\hat{x}_{1i})^2}{\sigma_x^2}+\frac{(y_{1i}-\hat{y}_{1i})^2}{\sigma_y^2}\right] \tag{14}$$

where the σ elements are the estimated standard deviations for the measured

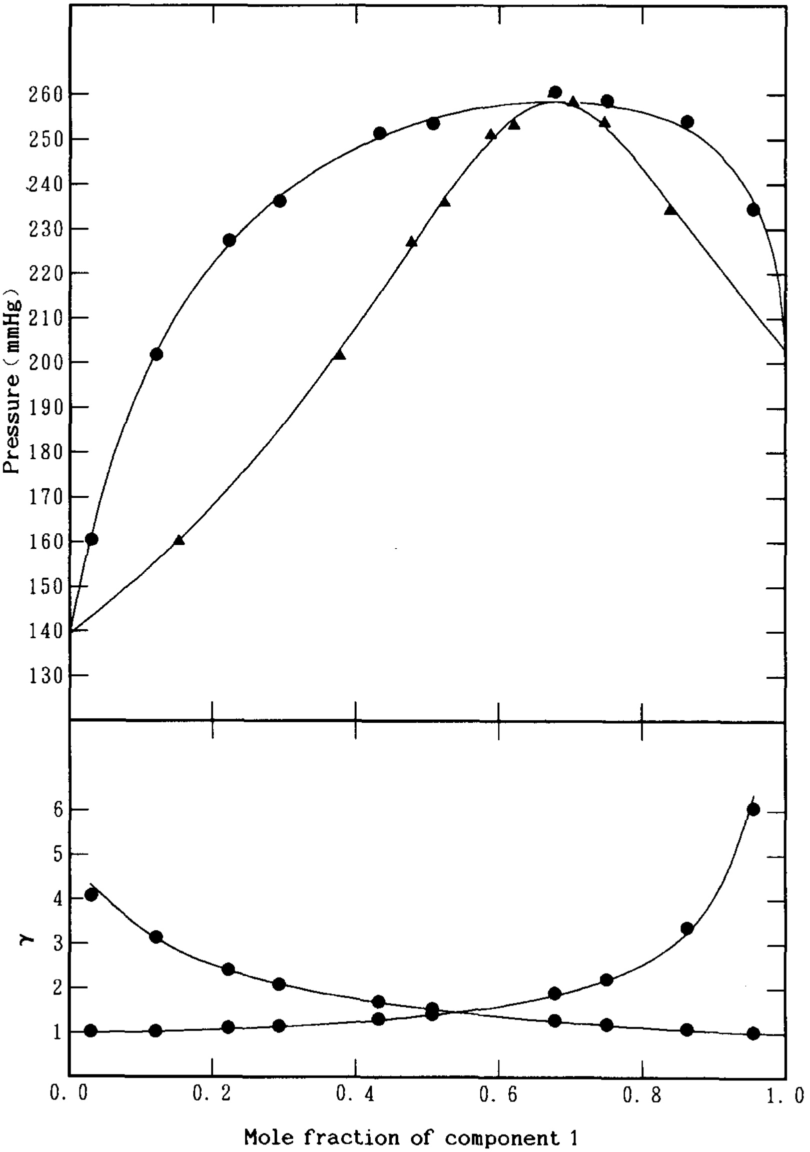

Fig. 2. Vapour–liquid equilibrium for methylcyclohexane(1)–2-butanol(2) at 60 °C. ▲, ●, Experimental; ———, calculated from the UNIQUAC associated-solution model.

variables, calculated as follows: pressure, $\sigma_P = 1$ mmHg; temperature, $\sigma_T = 0.05\,^\circ C$; liquid-phase and vapour-phase mole fractions, $\sigma_x = 0.001$ and $\sigma_y = 0.003$. A circumflex denotes the most probable calculated value corresponding to each observed variable. The resulting parameters of the two models for the binary systems of methylcyclohexane with these five alcohols

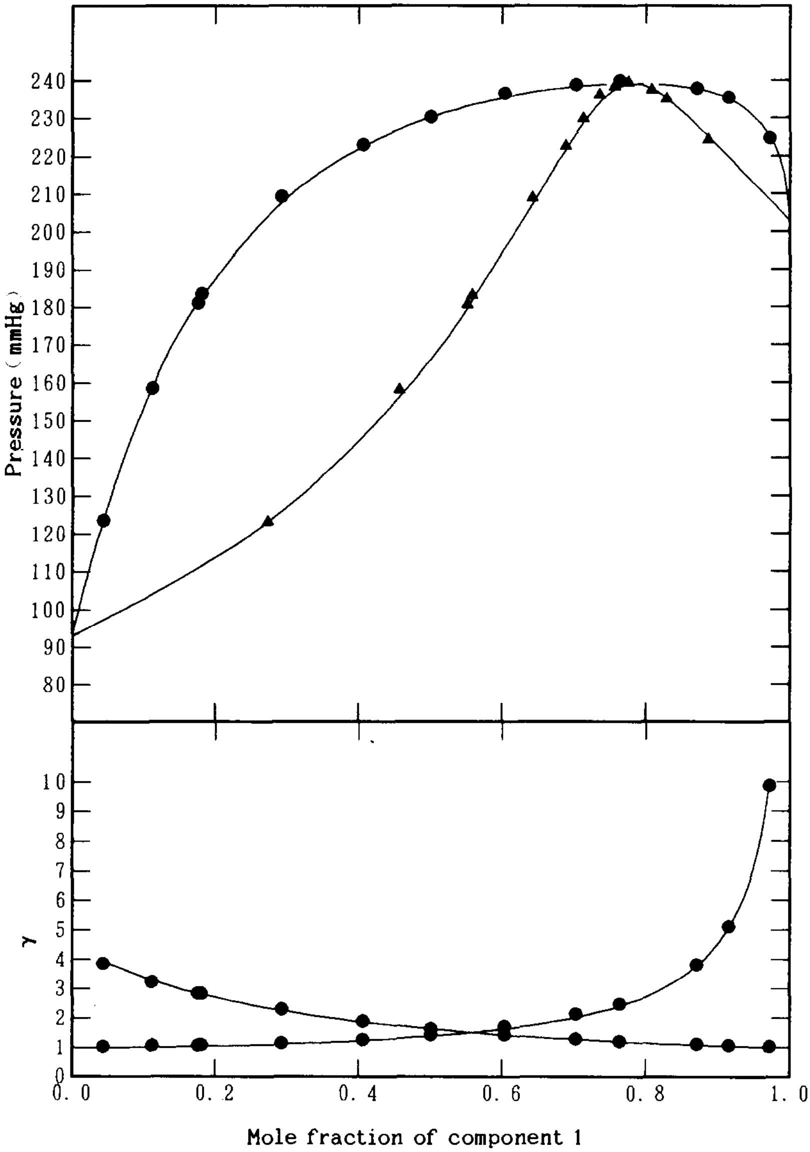

Fig. 3. Vapour-liquid equilibrium for methylcyclohexane(1)-2-methyl-1-propanol(2) at 60 ° C. ▲, ●, Experimental; ———, calculated from the UNIQUAC associated-solution model.

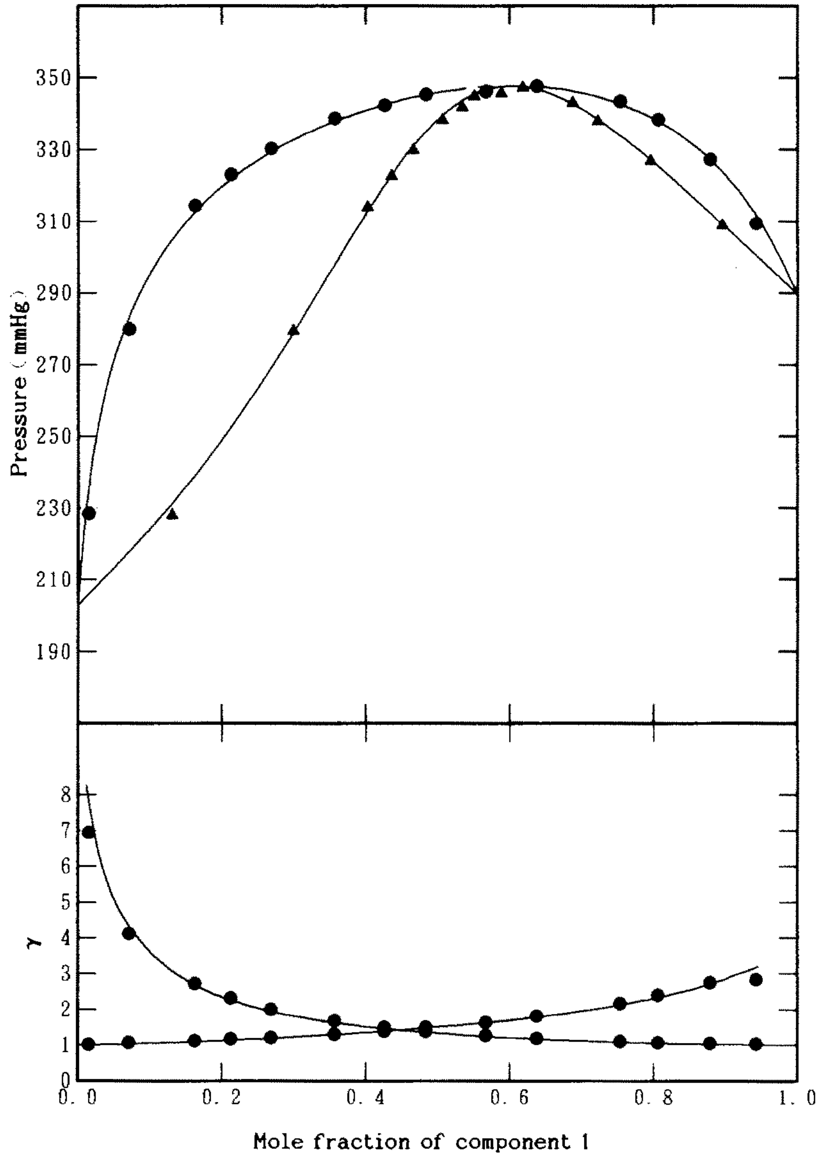

Fig. 4. Vapour–liquid equilibrium for 2-methyl-2-propanol(2)–methylcyclohexane(2) at 60 ° C. ▲, ●, Experimental ———, calculated from the UNIQUAC associated-solution model.

are shown in Table 4, together with the root-mean-square deviations between the experimental and calculated values. Except for the methylcyclohexane-2-butanol system, the overall fits of the models to the experimental data are comparable. Figures 1–5 show comparisons between the

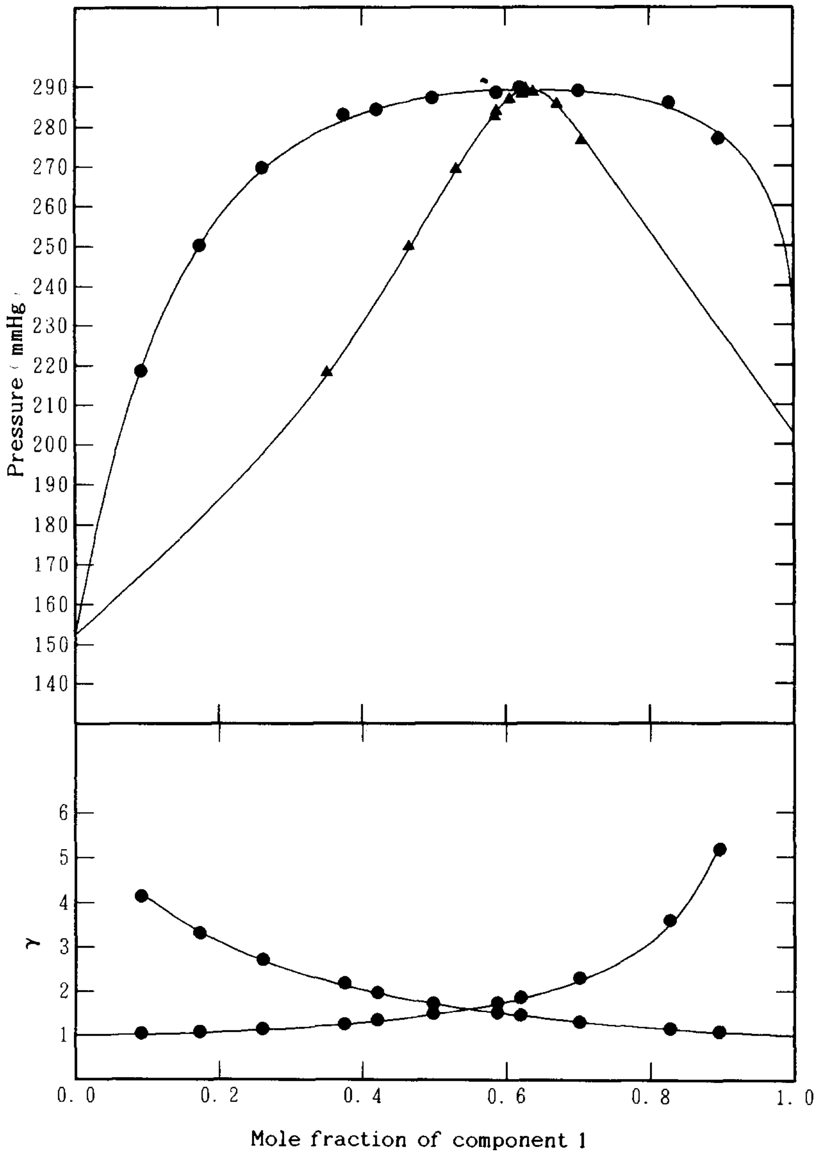

Fig. 5. Vapour–liquid equilibrium for methylcyclohexane(1)–1-propanol(2) at 60 °C. ▲, ●, Experimental ———, calculated from the UNIQUAC associated-solution model.

measured data and calculated results derived from the UNIQUAC associated-solution model.

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