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THERMODYNAMICS OF ALCOHOL SOLUTIONS. PHASE EQUILIBRIA AND EXCESS MOLAR ENTHALPIES OF MIXTURES CONTAINING TWO ALCOHOLS

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ABSTRACT

The association constant and the enthalpy of hydrogen-bond formation for pure aliphatic alcohols have been determined from the vapor pressures of the pure alcohols as a function of temperature using Brandani's method, based on the homomorph concept which uses ethers instead of saturated hydrocarbons as the homomorphs of alcohols. The results of phase equilibrium and excess enthalpy data reduction obtained with the new association parameters are comparable with those derived from Brandani's values.

INTRODUCTION

A new method, based on an association model, was presented by Brandani [1] for determining the enthalpy of hydrogen-bond formation and the equilibrium association constant for pure liquid compounds. The method needed the experimental vapor pressures of the pure liquids as a function of temperature and adopted the saturated hydrocarbons as the homomorphs of pure hydrogen-bonded liquids. Brandani's association parameters have been used in the UNIQUAC associated-solution theory to reduce vapor–liquid and liquid–liquid equilibrium and excess molar enthalpy data for associated solutions [2–6]. An alternative method [7], based on the Flory–Huggins relation, used the isomeric ether as the alcohol's homomorph and assumed the volume change of mixing. Association parameters derived from the latter method should not be used in the UNIQUAC associated-solution theory, because the theory assumes no volume change.

This paper presents the association constant and the enthalpy of hydrogen-bond formation for pure aliphatic alcohols derived from Brandani's procedure, which adopts the ether as the alcohol's homomorph. The new association parameters will be used with the revised UNIQUAC associated-solution theory [4–6] to analyze vapor–liquid and liquid–liquid equilibrium and excess molar enthalpy data for mixtures including two alcohols.

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ESTIMATION OF ASSOCIATION PARAMETERS FOR ALIPHATIC ALCOHOLS

I assume that the pure alcohol forms linear polymers by consecutive reactions expressed as $A_i + A_1 = A_{i+1}$ and the equilibrium association constant K_A for these reactions is defined by

$$K_A = \frac{\Phi^0_{A_{i+1}}}{\Phi^0_{A_i}\Phi^0_{A_1}} \frac{i}{i+1} \text{ for all } i \geqslant 1 \tag{1}$$

K_A is independent of the degree of association. The enthalpy of hydrogen-bond formation h_A fixes the temperature dependence of the association constant by the van't Hoff relation and is assumed to be temperature-independent.

According to Brandani's method [1], the vapor pressure of the pure alcohol is calculated by

$$P^s_A = \gamma^0_{A_1} x^0_{A_1} P^s_h \exp\left[\left(P^s_A - P^s_h\right)\left(v^L_A - B^F_A\right)/RT\right] \tag{2}$$

where $\gamma^0_{A_1}$ is the activity coefficient of the pure alcohol monomer adjusted to zero pressure, $x^0_{A_1}$ is the mole fraction of the monomer in the pure alcohol, P^s_h is the vapor pressure of the hypothetical fluid, v^L_A is the molar pure alcohol volume estimated from the modified Rackett equation [8] and B^F_A is the free contribution to the second virial coefficient calculated from the correlation of Hayden and O'Connell [9] with the related parameters given by Prausnitz et al. [10].

$\gamma^0_{A_1}$ is expressed as

$$\ln \gamma^0_{A_1} = \ln \frac{\Phi^0_{A_1}}{x^0_{A_1}} + 1 - \frac{\Phi^0_{A_1}}{x^0_{A_1}} \tag{3}$$

where the segment fraction of the pure alcohol monomer ($\Phi^0_{A_1}$) and $x^0_{A_1}$ are given as follows

$$\Phi^0_{A_1} = \frac{1 + 2K_A - (1 + 4K_A)^{1/2}}{2K_A^2} \tag{4}$$

$$x^0_{A_1} = 1 - K_A \Phi^0_{A_1} \tag{5}$$

The vapor pressures of the ethers are used to estimate P^s_h. Ambrose et al. [11] have measured the vapor pressures of some ethers as the homomorph of the alcohol: dimethyl ether for ethanol; ethyl methyl ether for 1-propanol; propyl methyl ether for 1-butanol; isopropyl methyl ether for isobutanol; butyl methyl ether for 1-pentanol; decyl methyl ether for 1-undecanol. Ambrose et al. have given a general equation to represent their measured vapor pressure data for a number of ethers in terms of the effective carbon number in the ether n^*

$$\begin{aligned}\log_{10} P\ (\text{kPa}) = {} & 7.1972 + 0.1752n^* - (916.74 + 184.766n^*)T^{-1} \\ & - (9.6590 + 1.17110n^*)10^{-4}T \\ & - (1.34082 - 0.152687n^*)10^{-6}T^2\end{aligned} \tag{6}$$

TABLE 1

Results of the fit for vapor pressure data of alcohols

Substance	Temperature range (°C)	Absolute arithmetic mean deviation (Torr)
Methanol	1.7–60	0.89
Ethanol	19.6–75	0.58
1-Propanol	48.1–90	0.09
2-Propanol	52.3–80	0.06
1-Butanol	78.6–115	0.18
2-Butanol	67.7–95	0.25
iso-Butanol	69.9–105	0.24
tert-Butanol	56.8–80	0.23
1-Pentanol	74.8–135	0.66
1-Hexanol	52.2–155	1.01
1-Heptanol	63.6–175	1.04
1-Octanol	78.9–190	1.04
1-Nonanol	140.0–195	0.69
1-Decanol	170.0–230	0.55

and stated that if used with the values of n^* in table 4 of ref. 11, eqn. (6) reproduces the values obtained in the correlation for all the other compounds, including those whose properties were estimated, nearly as well.

The following values of n^* for ethers corresponding to other alcohols were used: 1 for methanol; 2.60 for 2-propanol, 3.605 for 2-butanol and 3.366 for tert-butanol are halves of those for diisopropyl ether, di-s-butyl ether and di-t-butyl ether, respectively. Values of n^* for 1-hexanol to 1-decanol were obtained by linear interpolation between 5.260 of butyl methyl ether for 1-pentanol and 11.3 of decyl methyl ether for 1-undecanol [11]: 6.267 for 1-hexanol; 7.273 for 1-heptanol; 8.280 for 1-octanol; 9.287 for 1-nonanol; 10.293 for 1-decanol.

K_A at 50°C and h_A for 14 aliphatic alcohols were calculated by minimizing the objective function defined by

$$F = \sum_{i=1}^{N} \left[P_{A,i}^{s}(\text{exp}) - P_{A,i}^{s}(\text{calc}) \right]^2 \qquad (7)$$

where eqn. (2) was used to calculate P_A^s(calc) and P_A^s(exp) was obtained from the Antoine equation [12] at each of 21 equally spaced points in the temperature range listed in Table 1, where the absolute average deviation between calculated and experimental vapor pressures are reported for 14 alcohols. Table 2 compares the association parameters obtained in this work with those estimated by Brandani [1]. The values of the enthalpy of hydrogen-bond formation obtained here are usually lower than Brandani's values

TABLE 2

Association parameters for alcohols

Substance	K_A (50°C)		$-h_A$ (kJ mol^{-1})	
	I [a]	II [b]	I	II
Methanol	173.9	125.1	25.4	23.6
Ethanol	110.4	103.2	25.9	23.6
1-Propanol	87.0	89.9	27.0	23.6
2-Propanol	49.1	71.9	26.4	23.9
1-Butanol	69.5	83.0	27.1	23.3
2-Butanol	31.1	57.7	25.9	22.6
iso-Butanol	50.6	67.0	26.0	23.0
tert-Butanol	23.1	30.5	25.9	21.5
1-Pentanol	47.7	67.8	24.5	22.8
1-Hexanol	40.8	59.6	24.9	22.4
1-Heptanol	40.7	49.8	25.9	22.1
1-Octanol	39.5	41.2	24.9	21.9
1-Nonanol		32.1		21.9
1-Decanol	36.8	25.3	20.3	21.8

[a] I, Brandani [1].
[b] II, This work.

and are comparable to the enthalpies of dilution of ethanol in saturated hydrocarbons at 25°C [13].

ASSOCIATION THEORY

The UNIQUAC associated-solution theory [4–6] gives the activity coefficient of any component in a mixture including two alcohols and the excess molar enthalpy of the mixture as follows.

Binary mixtures containing two alcohols

A and B stand for alcohols. The alcohol B associates linearly as does alcohol A. These two alcohols solvate each other to yield linear copolymers whose general formulas are $(A_iB_j)_k$, $A_l(B_jA_k)_l$, $(B_iA_j)_k$ and $B_l(A_jB_k)_l$, where the indices i, j, k and l can be any integers from 1 to infinity. I assume that the solvated species $(A_iB_j)_k$ is not identical with $(B_iA_j)_k$, because the last molecule of the former B has a free hydroxyl group and the last one of the latter A has it.

The activity coefficients of both components are expressed by

$$\ln \gamma_A = \ln\left(\frac{\Phi_{A_1}}{\Phi^0_{A_1} x_A}\right) + r_A\left(\frac{1}{V^0_A} - \frac{1}{V}\right) - \left(\frac{Z}{2}\right) q_A\left(\ln\frac{\Phi_A}{\theta_A} + 1 - \frac{\Phi_A}{\theta_A}\right)$$
$$+ q_A\left[-\ln(\theta_A + \theta_B\tau_{BA}) + \theta_B\left(\frac{\tau_{BA}}{\theta_A + \theta_B\tau_{BA}} - \frac{\tau_{AB}}{\theta_B + \theta_A\tau_{AB}}\right)\right] \tag{8}$$

$$\ln \gamma_B = \ln\left(\frac{\Phi_{B_1}}{\Phi^0_{B_1} x_B}\right) + r_B\left(\frac{1}{V^0_B} - \frac{1}{V}\right) - \left(\frac{Z}{2}\right) q_B\left(\ln\frac{\Phi_B}{\theta_B} + 1 - \frac{\Phi_B}{\theta_B}\right)$$
$$+ q_B\left[-\ln(\theta_B + \theta_A \tau_{AB}) + \theta_A\left(\frac{\tau_{AB}}{\theta_B + \theta_A \tau_{AB}} - \frac{\tau_{BA}}{\theta_A + \theta_B \tau_{BA}}\right)\right] \tag{9}$$

where the nominal segment fraction Φ, the nominal surface fraction θ, and the coefficient τ are given by

$$\Phi_A = r_A x_A / (r_A x_A + r_B x_B)$$
$$\Phi_B = r_B x_B / (r_A x_A + r_B x_B) \tag{10}$$
$$\theta_A = q_A x_A / (q_A x_A + q_B x_B)$$
$$\theta_B = q_B x_B / (q_A x_A + q_B x_B) \tag{11}$$
$$\tau_{BA} = \exp(-a_{BA}/T)$$
$$\tau_{AB} = \exp(-a_{AB}/T) \tag{12}$$

r and q are the pure-component structural parameters estimated by the method of Vera et al. [14] and the energy parameters, a_{BA} and a_{AB}, are obtained in fitting the theory to experimental phase equilibrium data.

The monomer segments fractions, Φ_{A_1} and Φ_{B_1}, are obtained from the following mass balance equations

$$\Phi_A = \bar{S}_A + \frac{r_A K_{AB} \bar{S}_A S_B}{(1 - r_A r_B K^2_{AB} S_A S_B)^2}$$
$$\times \left[2 + r_B K_{AB} S_A (2 - r_A r_B K^2_{AB} S_A S_B) + r_A K_{AB} S_B\right] \tag{13}$$
$$\Phi_B = \bar{S}_B + \frac{r_B K_{AB} S_A \bar{S}_B}{(1 - r_A r_B K^2_{AB} S_A S_B)^2}$$
$$\times \left[2 + r_A K_{AB} S_B (2 - r_A r_B K^2_{AB} S_A S_B) + r_B K_{AB} S_A\right] \tag{14}$$

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

$$\bar{S}_A = \Phi_{A_1} / (1 - K_A \Phi_{A_1})^2 \tag{15}$$
$$\bar{S}_B = \Phi_{B_1} / (1 - K_B \Phi_{B_1})^2 \tag{16}$$
$$S_A = \Phi_{A_1} / (1 - K_A \Phi_{A_1}) \tag{17}$$
$$S_B = \Phi_{B_1} / (1 - K_B \Phi_{B_1}) \tag{18}$$

The true molar volume of the binary mixture V is expressed as

$$\frac{1}{V} = \frac{S_A}{r_A} + \left(\frac{2}{r_A r_B K_{AB}} + \frac{S_A}{r_A} + \frac{S_B}{r_B}\right) \frac{r_A r_B K^2_{AB} S_A S_B}{(1 - r_A r_B K^2_{AB} S_A S_B)} + \frac{S_B}{r_B} \tag{19}$$

At pure alcohol states, $\Phi_{A_1}^0$ is given by eqn. (4). $\Phi_{B_1}^0$, V_A^0 and V_B^0 are obtained by

$$\Phi_{B_1}^0 = \frac{1 + 2K_B - (1 + 4K_B)^{1/2}}{2K_B^2} \tag{20}$$

$$1/V_A^0 = \left(1 - K_A\Phi_{A_1}^0\right)/r_A \tag{21}$$

$$1/V_B^0 = \left(1 - K_B\Phi_{B_1}^0\right)/r_B \tag{22}$$

The excess molar enthalpy of the mixture is given by

$$\begin{aligned} H^E = {} & h_A x_A\left(\frac{\overline{U}_A\Phi_{A_1}}{\Phi_A} - \overline{U}_A^0\Phi_{A_1}^0\right) + h_B x_B\left(\frac{\overline{U}_B\Phi_{B_1}}{\Phi_B} - \overline{U}_B^0\Phi_{B_1}^0\right) \\ & + \Biggl\{ h_A\Biggl[\frac{\overline{U}_A}{K_{AB}U_A}\left(\frac{x_B}{\Phi_B r_A} + \frac{x_A}{\Phi_A r_B}\right) + \frac{\overline{U}_A x_A\Phi_{A_1}}{\Phi_A}\left(2 - r_A r_B K_{AB}^2\Phi_{A_1}\Phi_{B_1}U_A U_B\right) \\ & + \frac{\overline{U}_A U_B x_B\Phi_{B_1}}{U_A\Phi_B}\Biggr] + h_B\Biggl[\frac{\overline{U}_B}{K_{AB}U_B}\left(\frac{x_B}{\Phi_B r_A} + \frac{x_A}{\Phi_A r_B}\right) \\ & + \frac{\overline{U}_B x_B\Phi_{B_1}}{\Phi_B}\left(2 - r_A r_B K_{AB}^2\Phi_{A_1}\Phi_{B_1}U_A U_B\right) + \frac{U_A\overline{U}_B x_A\Phi_{A_1}}{U_B\Phi_A}\Biggr] \\ & + h_{AB}\Biggl[\left(\frac{x_B}{\Phi_B r_A} + \frac{x_A}{\Phi_A r_B}\right)\frac{\left(1 + r_A r_B K_{AB}^2\Phi_{A_1}\Phi_{B_1}U_A U_B\right)}{K_{AB}} \\ & + 2\left(\frac{U_A x_A\Phi_{A_1}}{\Phi_A} + \frac{U_B x_B\Phi_{B_1}}{\Phi_B}\right)\Biggr]\Biggr\}\frac{r_A r_B K_{AB}^2\Phi_{A_1}\Phi_{B_1}U_A U_B}{\left(1 - r_A r_B K_{AB}^2\Phi_{A_1}\Phi_{B_1}U_A U_B\right)^2} \\ & - R\left[\frac{q_A x_A\theta_B}{(\theta_A + \theta_B\tau_{BA})}\frac{\partial\tau_{BA}}{\partial(1/T)} + \frac{q_B x_B\theta_A}{(\theta_B + \theta_A\tau_{AB})}\frac{\partial\tau_{AB}}{\partial(1/T)}\right] \end{aligned} \tag{23}$$

where $\overline{U}_A$, $\overline{U}_B$, U_A and U_B, respectively, are defined by

$$\overline{U}_A = K_A\Phi_{A_1}/\left(1 - K_A\Phi_{A_1}\right)^2 \tag{24}$$

$$\overline{U}_B = K_B\Phi_{B_1}/\left(1 - K_B\Phi_{B_1}\right)^2 \tag{25}$$

$$U_A = 1/\left(1 - K_A\Phi_{A_1}\right) \tag{26}$$

$$U_B = 1/\left(1 - K_B\Phi_{B_1}\right) \tag{27}$$

It is assumed that a_{BA} and a_{AB} are linearly dependent on temperature.

$$\begin{aligned} a_{BA} &= C_A + D_A(T - 273.15) \\ a_{AB} &= C_B + D_B(T - 273.15) \end{aligned} \tag{28}$$

Ternary mixtures containing two alcohols and one active nonassociating component

In the mixture exist associated species and solvated ones whose general forms are A_i, B_i, $(A_iB_j)_k$, $A_i(B_jA_k)_l$, $(B_iA_j)_k$, $B_i(A_jB_k)_l$, A_iC, $(A_iB_j)_kC$, $A_i(B_jA_k)_lC$, B_iC, $(B_iA_j)_kC$ and $B_i(A_jB_k)_lC$, where the indices i, j, k and l can go from 1 to infinity.

The activity coefficient of component I is

$$\ln\gamma_I = \ln\left(\frac{\Phi_{I_1}}{\Phi_{I_1}^0 x_I}\right) + \frac{r_I}{V_I^0} - \frac{r_I}{V} - \left(\frac{Z}{2}\right)q_I\left(\ln\frac{\Phi_I}{\theta_I} + 1 - \frac{\Phi_I}{\theta_I}\right)$$
$$+ q_I\left[1 - \ln\left(\sum_J \theta_J\tau_{JI}\right) - \sum_J \frac{\theta_J\tau_{IJ}}{\sum_K \theta_K\tau_{KJ}}\right] \qquad (29)$$

where Φ_I, θ_I, V_I^0, V and τ_{JI} are expressed as follows:

$$\Phi_I = r_I x_I \Big/ \sum_J r_J x_J \qquad (30)$$

$$\theta_I = q_I x_I \Big/ \sum_J q_J x_J \qquad (31)$$

$$1/V_I^0 = \left(1 - K_I\Phi_{I_1}^0\right)/r_I \qquad (32)$$

$$\frac{1}{V} = \frac{S_A}{r_A} + \frac{S_B}{r_B} + \left(\frac{2}{r_Ar_BK_{AB}} + \frac{S_A}{r_A} + \frac{S_B}{r_B}\right)\frac{r_Ar_BK_{AB}^2S_AS_B}{\left(1 - r_Ar_BK_{AB}^2S_AS_B\right)}$$
$$+ \frac{\Phi_{C_1}}{r_C}\left\{1 + r_CK_{AC}S_A + r_CK_{BC}S_B\right.$$
$$\left. + \left[\left(\frac{1}{r_BK_{AB}} + S_A\right)K_{AC} + \left(\frac{1}{r_AK_{AB}} + S_B\right)K_{BC}\right]\frac{r_Ar_Br_CK_{AB}^2S_AS_B}{\left(1 - r_Ar_BK_{AB}^2S_AS_B\right)}\right\} \qquad (33)$$

$$\tau_{JI} = \exp(-a_{JI}/T) \qquad (34)$$

$\Phi_{C_1}^0 = 1$ for component C, $\Phi_{A_1}^0$ and $\Phi_{B_1}^0$ are given by eqns. (4) and (20).

The monomer segment fractions, Φ_{A_1}, Φ_{B_1} and Φ_{C_1}, are numerically solved from the following mass balance equations:

$$\Phi_A = \left(1 + r_AK_{AC}\Phi_{C_1}\right)\bar{S}_A + \frac{r_AK_{AB}\bar{S}_AS_B}{\left(1 - r_Ar_BK_{AB}^2S_AS_B\right)^2}$$
$$\times\left\{2 + r_BK_{AB}S_A\left(2 - r_Ar_BK_{AB}^2S_AS_B\right) + r_AK_{AB}S_B\right.$$
$$+ \Phi_{C_1}\left[\left(r_AK_{AC} + r_BK_{BC}\right) + r_Ar_BK_{AB}K_{AC}S_A\right.$$
$$\left.\left.\times\left(2 - r_Ar_BK_{AB}^2S_AS_B\right) + r_Ar_BK_{AB}K_{BC}S_B\right]\right\} \qquad (35)$$

$$\begin{aligned}\Phi_B = {} & (1 + r_B K_{BC} \Phi_{C_1}) \bar{S}_B + \frac{r_B K_{AB} S_A \bar{S}_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)^2} \\ & \times \bigl\{ 2 + r_A K_{AB} S_B (2 - r_A r_B K_{AB}^2 S_A S_B) + r_B K_{AB} S_A \\ & + \Phi_{C_1} \bigl[(r_A K_{AC} + r_B K_{BC}) + r_A r_B K_{AB} K_{BC} S_B \\ & \times (2 - r_A r_B K_{AB}^2 S_A S_B) + r_A r_B K_{AB} K_{AC} S_A \bigr] \bigr\} \end{aligned} \tag{36}$$

$$\begin{aligned}\Phi_C = \Phi_{C_1} \biggl\{ & 1 + r_C K_{AC} S_A + r_C K_{BC} S_B \\ & + \frac{r_A r_B r_C K_{AB}^2 S_A S_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)} \left[\frac{K_{AC}}{r_B K_{AB}} + \frac{K_{BC}}{r_A K_{AB}} + K_{AC} S_A + K_{BC} S_B \right] \biggr\} \end{aligned} \tag{37}$$

The excess molar enthalpy of the mixture is expressed as

$$\begin{aligned} H^E = {} & h_A x_A \left(\frac{\bar{U}_A \Phi_{A_1}}{\Phi_A} - \bar{U}_A^0 \Phi_{A_1}^0 \right) + h_B x_B \left(\frac{\bar{U}_B \Phi_{B_1}}{\Phi_B} - \bar{U}_B^0 \Phi_{B_1}^0 \right) \\ & + (h_A \bar{U}_A + h_{AC} U_A) \frac{r_A K_{AC} \Phi_{C_1} x_A \Phi_{A_1}}{\Phi_A} \\ & + (h_B \bar{U}_B + h_{BC} U_B) \frac{r_B K_{BC} \Phi_{C_1} x_B \Phi_{B_1}}{\Phi_B} \\ & + \Biggl(h_A \biggl\{ \frac{\bar{U}_A}{K_{AB} U_A} \left(\frac{x_B}{r_A \Phi_B} + \frac{x_A}{r_B \Phi_A} \right) + \frac{\bar{U}_A x_A \Phi_{A_1}}{\Phi_A} (2 - r_A r_B K_{AB}^2 \Phi_{A_1} \Phi_{B_1} U_A U_B) \\ & + \frac{\bar{U}_A U_B x_B \Phi_{B_1}}{U_A \Phi_B} + \Phi_{C_1} \biggl[\left(\frac{r_B K_{BC} x_B}{r_A K_{AB} \Phi_B} + \frac{r_A K_{AC} x_A}{r_B K_{AB} \Phi_A} \right) \frac{\bar{U}_A}{U_A} \\ & + \frac{r_A K_{AC} \bar{U}_A x_A \Phi_{A_1}}{\Phi_A} (2 - \mathrm{r}_A r_B K_{AB}^2 \Phi_{A_1} \Phi_{B_1} U_A U_B) + \frac{r_B K_{BC} \bar{U}_A U_B x_B \Phi_{B_1}}{U_A \Phi_B} \biggr] \biggr\} \\ & + h_B \biggl\{ \frac{\bar{U}_B}{K_{AB} U_B} \left(\frac{x_B}{r_A \Phi_B} + \frac{x_A}{r_B \Phi_A} \right) + \frac{\bar{U}_B x_B \Phi_{B_1}}{\Phi_B} (2 - r_A r_B K_{AB}^2 \Phi_{A_1} \Phi_{B_1} U_A U_B) \\ & + \frac{U_A \bar{U}_B x_A \Phi_{A_1}}{U_B \Phi_A} + \Phi_{C_1} \biggl[\left(\frac{r_B K_{BC} x_B}{r_A K_{AB} \Phi_B} + \frac{r_A K_{AC} x_A}{r_B K_{AB} \Phi_A} \right) \frac{\bar{U}_B}{U_B} \\ & + \frac{r_B K_{BC} \bar{U}_B x_B \Phi_{B_1}}{\Phi_B} (2 - r_A r_B K_{AB}^2 \Phi_{A_1} \Phi_{B_1} U_A U_B) + \frac{r_A K_{AC} \bar{U}_B U_A x_A \Phi_{A_1}}{U_B \Phi_A} \biggr] \biggr\} \\ & + h_{AB} \biggl\{ \left(\frac{x_B}{r_A \Phi_B} + \frac{x_A}{r_B \Phi_A} \right) \frac{(1 + r_A r_B K_{AB}^2 \Phi_{A_1} \Phi_{B_1} U_A U_B)}{K_{AB}} \\ & + 2 \left(\frac{U_A x_A \Phi_{A_1}}{\Phi_A} + \frac{U_B x_B \Phi_{B_1}}{\Phi_B} \right) \end{aligned}$$

$$\begin{aligned}
&+\Phi_{C_1}\Bigg[\Bigg(\frac{r_B K_{BC} x_B}{r_A \Phi_B} + \frac{r_A K_{AC} x_A}{r_B \Phi_A}\Bigg) \\
&\times \frac{\big(1 + r_A r_B K_{AB}^2 \Phi_{A_1} \Phi_{B_1} U_A U_B\big)}{K_{AB}} \\
&+2\Bigg(\frac{r_A K_{AC} U_A x_A \Phi_{A_1}}{\Phi_A} + \frac{r_B K_{BC} U_B x_B \Phi_{B_1}}{\Phi_B}\Bigg)\Bigg]\Bigg\} \\
&+\Bigg[h_{AC} r_A K_{AC} \Phi_{C_1}\Bigg(\frac{U_A x_A \Phi_{A_1}}{\Phi_A} + \frac{x_A}{r_A K_{AB} \Phi_A}\Bigg) + h_{BC} r_B K_{BC} \Phi_{C_1} \\
&\times \Bigg(\frac{U_B x_B \Phi_{B_1}}{\Phi_B} + \frac{x_B}{r_A K_{AB} \Phi_B}\Bigg)\Bigg]\big(1 - r_A r_B K_{AB}^2 \Phi_{A_1} \Phi_{B_1} U_A U_B\big)\Bigg) \\
&\times \frac{r_A r_B K_{AB}^2 \Phi_{A_1} \Phi_{B_1} U_A U_B}{\big(1 - \mathrm{r}_A r_B K_{AB}^2 \Phi_{A_1} \Phi_{B_1} U_A U_B\big)^2} - R \sum_I q_I x_I \frac{\sum_J \theta_J \frac{\partial \tau_{JI}}{\partial (1/T)}}{\sum_J \theta_J \tau_{JI}} \qquad (38)
\end{aligned}$$

where a_{JI} is expressed by

$$a_{JI} = C_I + D_I (T - 273.15) \qquad (39)$$

CALCULATED RESULTS

Binary mixtures

The excess molar enthalpies of binary mixtures containing normal aliphatic alcohols are positive (heat is absorbed) and those of some binary mixtures of normal and branched alcohols are negative (heat is evolved). The theory is able to reproduce these data as shown below. Table 3 shows the binary calculated results for alcohol–alcohol mixtures obtained by use of several sets of K_{AB} and h_{AB} without addition of the energy parameters and some of the results are compared with experimental values in Figs. 1 and 2. These figures indicate that the experimental data of methanol–2-propanol and ethanol–1-pentanol mixtures are reproduced with only selected sets of K_{AB} and h_{AB} and this is not the case for methanol–1-butanol, where additional energy parameters should be included for the accurate correlation of the experimental data.

Vapor–liquid equilibrium data reduction was carried out by use of the thermodynamic equation

$$\phi_I y_I P = \gamma_I x_I \phi_I^s P_I^s \exp\big[v_I^L (P - P_I^s)/RT\big] \qquad (40)$$

where y, P, P^s and R are the vapor-phase mole fraction, total pressure,

TABLE 3

Results of fitting the UNIQUAC associated-solution theory to excess molar enthalpies for binary alcohol–alcohol mixtures at 25°C with the chemical contribution term alone

Mixture (A–B)	K_{AB}(50°C)	$-h_{AB}$ (kJ mol^{-1})	Absolute arith. mean deviation (J mol^{-1})	Ref.
Methanol–ethanol	83	23.6	1.28	15
	96	23.5	1.68	
	104	23.45	2.64	
	112	23.4	3.61	
Methanol–1-propanol	58	23.6	6.66	15
	67	23.5	4.58	
Methanol–2-propanol	76	23.75	3.25	16
	77	23.75	3.75	
	82	23.70	3.14	
Ethanol–1-propanol	48	23.6	0.72	15
Ethanol–1-pentanol	33	23.2	3.44	17
1-Propanol–1-pentanol	28	23.2	1.45	18
1-Butanol–2-butanol	33	22.9	3.58	19

pure-component vapor pressure and gas constant. The fugacity coefficients, ϕ_I and ϕ_I^s, were calculated from the volume-explicit equation of state truncated after the second term. The second virial coefficients were estimated from the method of Hayden and O'Connell [9]. Pure-component vapor pressures were calculated from the Antoine equation whose parameters were taken from the literature [20,21].

The computer program used, based on the maximum likelihood principle, was similar to that described by Prausnitz et al. [10]. The standard deviations in the measured variables were taken as $\sigma_P = 1.0$ Torr, $\sigma_T = 0.05$ K, $\sigma_x = 0.001$ and $\sigma_y = 0.003$.

Parameter estimation from mutual solubilities was performed by solving eqn. (41) for any component I.

$$(x_I\gamma_I)^{\mathrm{I}} = (x_I\gamma_I)^{\mathrm{II}} \qquad (41)$$

where the indices, I and II, represent equilibrium liquid phases.

Table 4 lists the values of the solvation equilibrium constants and enthalpies of complex formation used in binary and ternary phase equilibrium and excess enthalpy data calculations.

Table 5 presents the calculated result of binary phase equilibrium data reduction. In the correlation of vapor–liquid equilibria for alcohol–alcohol mixtures, various values of K_{AB} were used with or without the energy parameters. For a fixed value of K_{AB} the results obtained with the energy parameters are better than those without the energy parameters. Many sets of values of K_{AB} and the energy parameters can reduce the experimental data of these mixtures with good accuracy. Table 6 gives the calculated

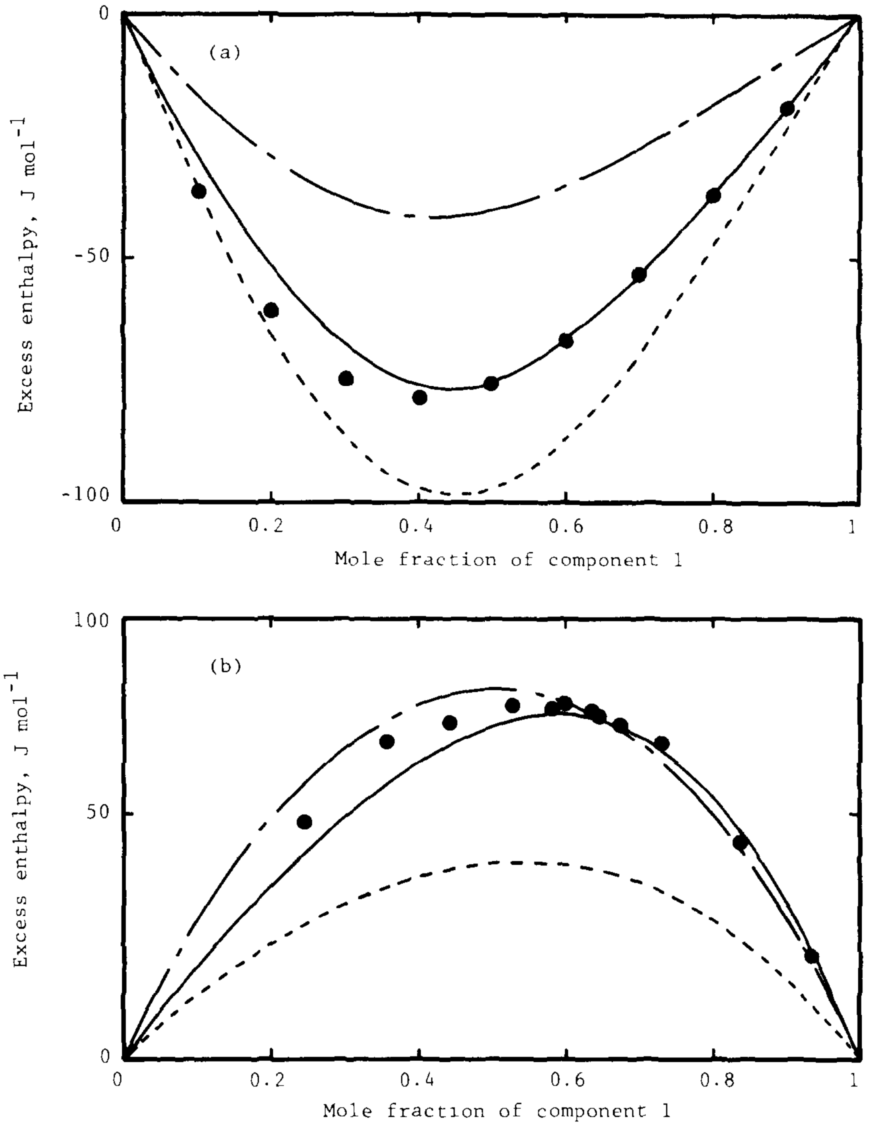

Fig. 1. Excess molar enthalpies for (a) methanol (1)–2-propanol (2) and (b) ethanol (1)–1-pentanol (2) at 25°C. Experimental (●): (a) ref. 16; (b) ref. 17. Calculated: (a) (- — - — -) $K_{AB} = 70(50°C)$ and $h_{AB} = -23.75$ kJ mol^{-1}; (———) $K_{AB} = 76(50°C)$ and $h_{AB} = -23.75$ kJ mol^{-1}; (- - - - - -) $K_{AB} = 80(50°C)$ and $h_{AB} = -23.75$ kJ mol^{-1}; (b) (- — - — -) $K_{AB} = 33(50°C)$ and $h_{AB} = -23.2$ kJ mol^{-1}; (———) $K_{AB} = 43(50°C)$ and $h_{AB} = -23$ kJ mol^{-1}; (- - - - - -) $K_{AB} = 36(50°C)$ and $h_{AB} = -23.2$ kJ mol^{-1}.

results of excess molar enthalpy. The accuracy of the correlation studied in this paper is the same as that obtained in previous papers [4–6], indicating that the results of data reduction are not sensitive to used association parameters.

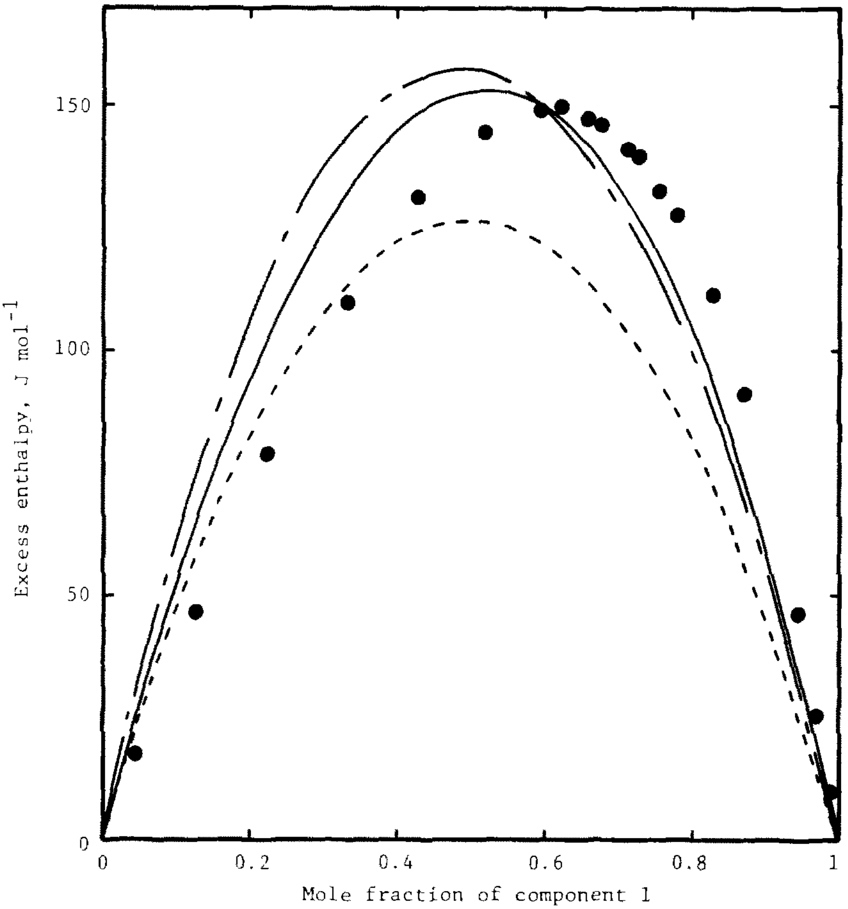

Fig. 2. Excess molar enthalpies for methanol (1)–1-butanol (2) at 25°C. Experimental (●), ref. 31. Calculated: (— - —) $K_{AB} = 46$(50°C) and $h_{AB} = -23.45$ kJ mol^{-1}; (———) $K_{AB} = 56$(50°C) and $h_{AB} = -23.3$ kJ mol^{-1}; (------) $K_{AB} = 50$(50°C) and $h_{AB} = -23.45$ kJ mol^{-1}.

TABLE 4

Solvation constants and enthalpies of complex formation

Mixture (A–B)	K_{AB} (50°C)	$-h_{AB}$ (kJ mol^{-1})
Methanol–benzene	2	8.3
Methanol–chlorobenzene	3(55°C)	
Methanol–ethanol	110	23.6
Methanol–2-propanol	80	23.75
Ethanol–benzene	2	8.3
2-Propanol–chlorobenzene	2(55°C)	
2-Propanol–benzene	1.8	8.3

TABLE 5

Binary calculated results obtained from phase equilibrium data reduction

Mixture (A–B)	Temp. (°C)	No. of data points	Root-mean square deviations				Parameters (K)		K_{AB} (50°C)	$-h_{AB}$ (kJ mol^{-1})	Ref.
			δP (Torr)	δT (°C)	δx ($\times 10^3$)	δy ($\times 10^3$)	a_{AB}	a_{BA}			
Methanol–ethanol	25	12	1.31			5.2	0	0	80	23.6	22
			0.26	0.00	0.1	1.6	−88.90	84.76	80	23.6	
			0.42	0.00	0.1	1.2	−29.46	127.90	100	23.6	
			0.56	0.00	0.2	1.8	−6.83	157.09	110[a]	23.6	
			0.76	0.00	0.3	2.6	17.67	183.81	120	23.6	
Methanol–2-propanol	55	20	6.36			10.6	0	0	55	23.75	23
			3.18	0.01	0.1	5.4	−115.44	115.77	55	23.75	
			1.78	0.07	0.9	3.9	−80.03	188.12	70	23.75	
			1.78	0.07	0.9	3.9	−73.03	226.46	76	23.75	
			1.79	0.07	0.9	3.9	−65.78	249.77	80[a]	23.75	
			2.12	0.09	1.1	5.6	−19.74	337.96	100	23.75	
Methanol–benzene	25	26	2.60	0.00	0.9		−132.67	282.01	2	8.3	22
Methanol–chlorobenzene	55	13	2.80	0.12	1.2	4.1	−98.99	278.70	3(55°C)		24
Ethanol–benzene	25	11	0.64	0.00	0.1	5.5	−16.14	97.68	2	8.3	25
Ethanol–cyclohexane	20	7	0.76	0.01	0.3	3.4	98.57	−25.65			23
Ethanol–methylcyclohexane	35	8	0.27	0.00	0.4	2.1	47.80	2.70			23
2-Propanol–chlorobenzene	55	12	0.91	0.00	0.3	3.4	107.86	−10.49	2(55°C)		26
2-Propanol–cyclohexane	50	9	1.32	0.04	0.5	5.6	226.62	1.32			27
2-Propanol–*n*-hexane	55.06	24	2.70	0.00	0.9	3.3	240.51	−141.27			22
Methanol–cyclohexane	25	MS[b]					−17.05	119.73			28
Methanol–*n*-hexane	5	MS					25.23	71.79			29
	25	MS					−12.30	103.04			29
Methanol–methylcyclohexane	25	MS					−11.12	96.57			30

[a] Parameters used for ternary-phase equilibrium calculations.

[b] MS = mutual solubilities.

TABLE 6

Binary results of fitting the UNIQUAC associated-solution theory to excess molar enthalpies at 25 °C

Mixture (A–B)	No. of data points	Abs. arith. mean dev. (J mol^{-1})	Parameters				Ref.
			C_A (K)	C_B (K)	D_A	D_B	
Methanol–2-propanol	9	3.06	−18.43	16.07	0.0917	−0.1300	16
Methanol–1-butanol	19	0.43	−403.10	−2739.51	−2.3967	−9.5995 [a]	31
Ethanol–1-propanol	15	0.92	0	0	0	0	15
Ethanol–1-pentanol	13	3.44	0	0	0	0	17
Ethanol–1-octanol	20	0.90	1460.98	−303.61	7.9059	−3.1476	15
Ethanol–1-decanol	19	3.84	895.91	−2163.14	−0.7315	−6.1113	15
1-Propanol–1-pentanol	25	1.45	0	0	0	0	18
1-Propnaol–1-octanol	20	0.51	1428.67	−248.05	5.9498	−1.6182	15
1-Propanol–1-decanol	19	1.70	1160.52	−2072.92	1.8651	−6.6044	15
Ethanol–benzene	10	2.34	945.67	74.04	2.2439	0.4423	32
Ethanol–cyclohexane	20	3.52	1084.41	−1618.85	−8.4259	0.9263	33
Ethanol–*n*-heptane	12	8.57	1034.70	−130.52	11.3691	−6.0782	34
Ethanol–*n*-octane	12	4.37	2708.01	1121.96	13.2482	1.7575	34
1-Propanol–benzene	10	6.75	597.52	650.85	1.4091	2.4636	32
1-Propanol–cyclohexane	18	4.45	1021.92	−1203.49	0.5716	−3.1462	33
1-Propanol–*n*-heptane	13	7.00	348.66	−120.53	3.7964	−3.0304	34
1-Propanol–*n*-octane	13	6.35	1744.47	−465.59	7.7906	−2.8696	34
1-Propanol–*n*-tetradecane	14	6.97	842.19	−300.53	12.7537	−7.6121	34
1-Pentanol–*n*-heptane	14	12.31	1963.77	−1127.10	6.9573	−4.7539	34
1-Pentanol–*n*-octane	13	14.71	3478.33	−366.69	12.7384	−1.8188	34
1-Pentanol–*n*-tetradecane	13	9.30	1195.12	−834.74	9.6735	−6.7607	34
1-Octanol–*n*-heptane	20	6.10	1985.54	−554.65	8.4362	−2.8361	35
1-Octanol–*n*-octane	14	12.76	446.09	−1394.68	0.6522	−4.6038	34
1-Octanol–*n*-tetradecane	14	19.01	972.64	574.62	4.3819	1.0627	34
1-Decanol–*n*-heptane	19	5.06	2010.37	−797.41	10.2476	−4.1062	36
1-Decanol–*n*-octane	20	7.62	197.57	−1002.12	−1.0495	−2.1846	36
1-Decanol–*n*-tetradecane	14	18.44	1022.79	−99.04	6.3350	−2.1591	34

[a] $K_{AB} = 50(50\,°C)$ and $h_{AB} = -23.45$ kJ mol^{-1}.

Ternary mixtures

Table 7 shows the ternary predicted results of excess molar enthalpies for 18 mixtures containing two alcohols and one saturated hydrocarbon and one

TABLE 7

Predicted results of excess molar enthalpies for ternary mixtures containing two alcohols and one hydrocarbon at 25 °C

Mixture	No. of data points	Abs. arith. mean deviations		Ref.
		ΔH^E (J mol^{-1})	$\Delta H^E/H^E$ (%)	
Ethanol–1-propanol–cyclohexane	92	4.59	1.88	33
Ethanol–1-propanol–*n*-heptane	32	15.01	3.65	37
Ethanol–1-pentanol–*n*-heptane	35	13.59	4.86	37
Ethanol–1-octanol–*n*-heptane	30	5.82	1.86	37
Ethanol–1-decanol–*n*-heptane	30	7.23	2.04	37
Ethanol–1-propanol–*n*-octane	30	5.80	1.36	37
Ethanol–1-pentanol–*n*-octane	30	18.94	4.86	37
Ethanol–1-octanol–*n*-octane	30	19.03	4.84	37
Ethanol–1-decanol–*n*-octane	30	15.14	3.78	37
1-Propanol–1-pentanol–*n*-heptane	30	8.25	2.86	37
1-Propanol–1-octanol–*n*-heptane	35	9.98	3.64	37
1-Propanol–1-decanol–*n*-heptane	30	8.65	2.24	37
1-Propanol–1-pentanol–*n*-octane	37	12.32	3.00	37
1-Propanol–1-octanol–*n*-octane	30	7.08	1.93	37
1-Propanol–1-decanol–*n*-octane	30	7.60	1.74	37
1-Propanol–1-pentanol–*n*-tetradecane	30	6.00	1.80	37
1-Propnaol–1-octanol–*n*-tetradecane	35	14.62	3.47	37
1-Propanol–1-decanol–*n*-tetradecane	30	11.84	2.36	37
Ethanol–1-propanol–benzene	59	7.49	1.22	6
Overall mean deviation		10.47	2.81	

TABLE 8

Ternary predicted results of vapor–liquid equilibria obtained from binary parameters

Mixture	Temp. (°C)	No. of data points	Absolute arithmetic mean deviations			Ref.
			Δy ($\times 10^3$)	ΔP (Torr)	$\Delta P/P$ (%)	
Methanol–ethanol–benzene	25	24	6.4 6.7 8.3	3.7	2.6	38
Methanol–2-propanol–chlorobenzene	55	15	6.7 6.2 4.9	5.1	1.7	26

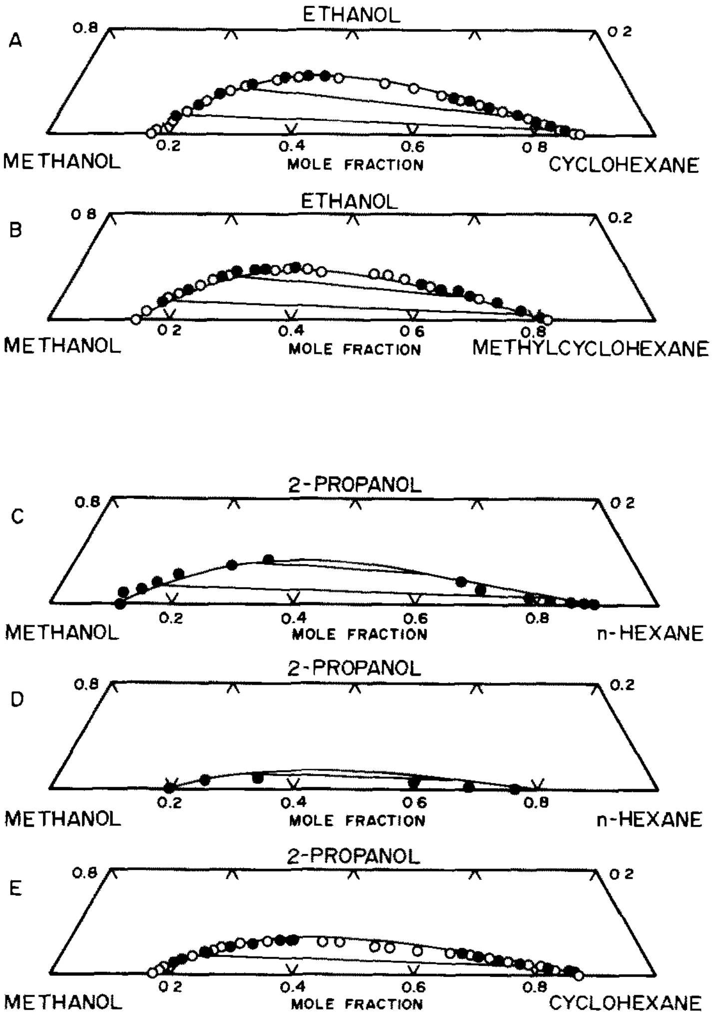

Fig. 3. Solubility envelopes for mixtures containing two alcohols and one saturated hydrocarbon. Experimental: tie-line (●); solubility (○). Calculated (———). (A) Methanol–ethanol–cyclohexane at 25°C [39]; (B) methanol–ethanol–methylcyclohexane at 25°C [30]; (C) methanol–2-propanol–*n*-hexane at 5°C [29]; (D) methanol–2-propanol–*n*-hexane at 25°C [29]; (E) methanol–2-propanol–cyclohexane at 25°C [40].

mixture including ethanol, 1-propanol and benzene. The overall mean deviation for 19 mixtures is 10.47 J mol^{-1}, which corresponds to 10.59 J mol^{-1} obtained in previous papers [5,6]. The predicted results of vapor–liquid equilibria for two mixtures are given in Table 7. The magnitude of the deviations is similar to that obtained previously [4]. The values of K_{AB} for alcohol–alcohol mixtures influence the calculated results of ternary liquid–liquid equilibria for mixtures containing two alcohols. The parameter set of $K_{AB} = 80$ at 50°C and non-zero values of the energy parameters for the methanol–ethanol mixture provided too large ternary solubility envelopes for methanol–ethanol–cyclohexane and methanol–ethanol–methylcylohexane mixtures. The parameter set of $K_{AB} = 110$ at 50 °C correctly reproduces liquid–liquid equilibria for these mixtures as shown in Fig. 3. Out of the parameters sets for the methanol–2-propanol mixture, the value of $K_{AB} = 80$ at 50 °C gives the best calculated results of ternary liquid–liquid equilibria for methanol–2-propanol–*n*-hexane and methanol–2-propanol–cyclohexane mixtures (Fig. 3).

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LIST OF SYMBOLS

A, B, C	alcohols and active nonassociating component
a_{IJ}	binary interaction parameter
B^F	free contribution to second virial coefficient
C_I, D_I	coefficients of eqn. (39)
F	objective function as defined by eqn. (7)
H^E	excess molar enthalpy
h_A, h_B	enthalpies of hydrogen-bond formation of alcohols A and B
h_{AB}, h_{AC}, h_{BC}	enthalpies of complex formation between unlike molecules
K_A, K_B	association constants of alcohols A and B
K_{AB}, K_{AC}, K_{BC}	solvation constants between unlike molecules
n^*	effective number of carbon atoms in an ether molecule
P	total pressure
P_I^s	saturated vapor pressure of pure component I
q_I	molecular geometric area parameter of pure component I
R	universal gas constant
r_I	molecular geometric volume parameter of pure component I
$\bar{S}_A$, $\bar{S}_B$	sums as defined by eqns. (15) and (16)
S_A, S_B	sums as defined by eqns. (17) and (18)
T	absolute temperature
$\bar{U}_A$, $\bar{U}_B$	quantities as defined by eqns. (24) and (25)
U_A, U_B	quantities as defined by eqns. (26) and (27)
V	true molar volume of alcohol mixture given by eqns. (19) or (33)
V_I^0	true molar volume of pure alcohol I given by eqn. (32)

v_I^L	molar liquid volume of pure component I
x_I	liquid-phase mole fraction of component I
y_I	vapor-phase mole fraction of component I
Z	lattice coordination number equal to 10

Greek letters

γ_I	activity coefficient of component I
θ_I	surface fraction of component I
σ_P, σ_T, σ_x, σ_y	standard deviations in pressure, temperature, liquid-phase mole fraction and vapor-phase mole fraction, respectively
τ_{IJ}	coefficient as defined by $\exp(-a_{IJ}/T)$
Φ_I	segment fraction of component I
Φ_{I_1}	monomer segment fraction of component I
ϕ_I	vapor-phase fugacity coefficient of component I
ϕ_I^s	vapor-phase fugacity coefficient of pure component I at T and P_I^s

Subscripts

A, B, C	alcohols and active nonassociating component
A_1, B_1, C_1	monomers of components A, B and C
A_i, B_i	i-mers of alcohols
AB, AC, BC	binary complexes
A_iB_jC	complex containing i molecules of alcohol A, j molecules of alcohol B and one molecule of component C
A_iC	complex containing i molecules of alcohol A and one molecule of component C
B_iC	complex containing i molecules of alcohol B and one molecule of component C
h	hypothetical fluid
I, J, K	components I, J and K
i, j, k, l	i, j, k and l-mers of alcohols or indices

Subscript

^{0}	pure-liquid reference state

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