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THERMODYNAMICS OF SOLUTIONS OF BUTANOLS IN HYDROCARBONS *

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ABSTRACT

The spectroscopic and thermodynamic properties of solutions of butanols in hydrocarbons are correlated by means of the association model of Nagata and Tamura, which includes four association constants for open-chain and cyclic hydrogen-bonded groups and a solvation constant between the terminal hydroxyl group of the alcohol chains and a solvating molecule, with allowance for the NRTL equation. This model gives a good prediction of the excess molar enthalpies for 1-butanol + benzene + cyclohexane at 25 ° C.

INTRODUCTION

Stokes [1] has presented a chemical model based on mole fraction statistics to explain the spectroscopic and thermodynamic properties of dilute solutions of ethanol in cyclohexane. His model contains three association constants for open-chain groups of ethanol and one association constant for cyclic groups, with allowance for a van der Waals' interaction term. To make the model cover the whole range of composition, we have modified Stokes' model [2–4]. Our association model has been applied for the accurate description of the spectroscopic and thermodynamic properties of binary solutions of methanol, ethanol and propanols in nonassociating components and for the prediction of the thermodynamic properties of ternary solutions containing one of these aliphatic alcohols and two nonassociating components by use of binary parameters with good accuracy [2–4].

This paper shows how well our association model works to describe the spectroscopic and thermodynamic properties of solutions of butanols in hydrocarbons.

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* Dedicated to Professor W.W. Wendlandt on the occasion of his 60th birthday.

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ASSOCIATION MODEL

The model assumes that open chains of any length are formed by successive reactions and cyclic groups are present. The four association constants are defined as follows.

$$K_2 = x_{A_2}/x_{A_1}^2 \text{ for } A_1 + A_1 = A_2 \tag{1}$$

$$K_3 = x_{A_3}/x_{A_2}x_{A_1} \text{ for } A_2 + A_1 = A_3 \tag{2}$$

$$K = x_{A_{i+1}}/x_{A_i}x_{A_1} \text{ for } A_i + A_1 = A_{i+1},\ i \geqslant 3 \tag{3}$$

$$K_{cy} = \theta/i = x_{A_i}(\text{cyclic})/x_{A_i}(\text{open}) \text{ for } A_i(\text{open}) = A_i(\text{cyclic}),\ i > 4 \tag{4}$$

where θ is independent of i.

Furthermore the model includes a solvation equilibrium between the terminal hydroxyl group of associated alcohol open chains and one solvating molecule (B) and the cyclic hydrogen-bonded groups are assumed to be unsolvated as there are no free hydroxyl groups. The solvation constant is defined as

$$K_{AB} = x_{A_iB}/x_{A_i}x_{B_1} \text{ for } A_i(\text{open}) + B_1 = A_iB,\ i \geqslant 1 \tag{5}$$

The temperature dependence of the equilibrium constants should be given by

$$\begin{aligned} &\partial \ln K_2/\partial(1/T) = -h_2/R, &&\partial \ln K_3/\partial(1/T) = -(2h_A - h_2)/R \\ &\partial \ln K/\partial(1/T) = -h_A/R, &&\partial \ln \theta/\partial(1/T) = -h_A/R \\ &\partial \ln K_{AB}/\partial(1/T) = -h_{AB}/R \end{aligned} \tag{6}$$

The model assumes further that the excess molar Gibbs free energy is expressed as the sum of a chemical and a physical contribution. The chemical contribution is due to formation of chemical species and the physical contribution is given by the NRTL equation described by Renon and Prausnitz [5].

$$\begin{aligned} g^E &= g^E_{chem} + g^E_{phys} \\ &= x_A \ln\left(\frac{x_{A_1}}{x^*_{A_1}x_A}\right) + x_B \ln\left(\frac{x_{B_1}}{x_B}\right) \\ &\quad + x_A x_B\left[\frac{\tau_{BA}G_{BA}}{(x_A + x_B G_{BA})} + \frac{\tau_{AB}G_{AB}}{(x_B + x_A G_{AB})}\right] \end{aligned} \tag{7}$$

where

$$\begin{aligned} \tau_{BA} &= a_{BA}/T \\ \tau_{AB} &= a_{AB}/T \end{aligned} \tag{8}$$

$$\begin{aligned} G_{BA} &= \exp(-\alpha_{BA}\tau_{BA}) \\ G_{AB} &= \exp(-\alpha_{AB}\tau_{AB}) \end{aligned} \tag{9}$$

The nonrandomness parameter α_{BA} $(= \alpha_{AB})$ is taken as 0.3 [5]. a_{BA} and a_{AB} are adjustable binary energy parameters.

The activity coefficients of both components are derived by differentiating eqn. (7) with respect to x_A or x_B at constant temperature.

$$\ln \gamma_A = (\ln \gamma_A)_{chem} + (\ln \gamma_A)_{phys}$$

$$\ln \gamma_A = \ln\left(\frac{x_{A_1}}{x_{A_1}^* x_A}\right) + x_B^2\left[\frac{\tau_{BA} G_{BA}^2}{(x_A + x_B G_{BA})^2} + \frac{\tau_{AB} G_{AB}}{(x_B + x_A G_{AB})^2}\right] \tag{10}$$

$$\ln \gamma_B = (\ln \gamma_B)_{chem} + (\ln \gamma_B)_{phys}$$

$$\ln \gamma_B = \ln\left(\frac{x_{B_1}}{x_B}\right) + x_A^2\left[\frac{\tau_{AB} G_{AB}^2}{(x_B + x_A G_{AB})^2} + \frac{\tau_{BA} G_{BA}}{(x_A + x_B G_{BA})^2}\right] \tag{11}$$

The stoichiometric mole fraction x_A is related to the monomer mole fractions, x_{A_1} and x_{B_1}, in terms of the equilibrium constants.

$$\begin{aligned} x_A = \Big\{&(1 + K_{AB} x_{B_1})\left[x_{A_1} + 2K_2 x_{A_1}^2 + K_2 K_3 (3 - 2z) x_{A_1}^3/(1 - z)^2\right] \\ &+ K_2 K_3 K^2 \theta x_{A_1}^5/(1 - z)\Big\}/S \end{aligned} \tag{12}$$

where $z = K x_{A_1}$ and the stoichiometric sum S is given by

$$\begin{aligned} S = &(1 + K_{AB} x_{B_1})\left[x_{A_1} + 2K_2 x_{A_1}^2 + K_2 K_3 (3 - 2z) x_{A_1}^3/(1 - z)^2\right] \\ &+ K_2 K_3 K^2 \theta x_{A_1}^5/(1 - z) \\ &+ K_{AB} x_{B_1}\left[x_{A_1} + K_2 x_{A_1}^2 + K_2 K_3 x_{A_1}^3/(1 - z)\right] + x_{B_1} \end{aligned} \tag{13}$$

The sum of the mole fractions of all chemical species present should be unity.

$$\begin{aligned} &(1 + K_{AB} x_{B_1})\left[x_{A_1} + K_2 x_{A_1}^2 + K_2 K_3 x_{A_1}^3/(1 - z)\right] \\ &\quad - (K_2 K_3 \theta / K^3)\left[\ln(1 - z) + z + z^2/2 + z^3/3 + z^4/4\right] + x_{B_1} = 1 \end{aligned} \tag{14}$$

Equations (12)–(14) are used to obtain x_{A_1} and x_{B_1}.

At pure alcohol state eqn. (14) reduces to

$$\begin{aligned} &x_{A_1}^* + K_2 x_{A_1}^{*2} + K_2 K_3 x_{A_1}^{*3}/(1 - z^*) \\ &\quad - (K_2 K_3 \theta / K^3)\left[\ln(1 - z^*) + z^* + z^{*2}/2 + z^{*3}/3 + z^{*4}/4\right] = 1 \end{aligned} \tag{15}$$

where $z^* = K x_{A_1}^*$. Equation (15) is solved by iterating for $x_{A_1}^*$.

The excess molar enthalpy of the solution h^{E} is given as the sum of the chemical and physical contributions.

$$h^{\mathrm{E}} = h^{\mathrm{E}}_{\mathrm{chem}} + h^{\mathrm{E}}_{\mathrm{phys}} \tag{16}$$

$$\begin{aligned} h^{\mathrm{E}}_{\mathrm{chem}} = \Big\{ & \left(1 + K_{\mathrm{AB}} x_{\mathrm{B}_1}\right)\left[h_2 K_2 x^2_{\mathrm{A}_1} + h_{\mathrm{A}} K_2 K_3 x^3_{\mathrm{A}_1}(2-z)/(1-z)^2\right] \\ & + h_{\mathrm{A}} K_2 K_3 K^2 \theta x^5_{\mathrm{A}_1}/(1-z) \\ & + h_{\mathrm{AB}} K_{\mathrm{AB}} x_{\mathrm{B}_1}\left[x_{\mathrm{A}_1} + K_2 x^2_{\mathrm{A}_1} + K_2 K_3 x^3_{\mathrm{A}_1}/(1-z)\right]\Big\}/S \\ & - x_{\mathrm{A}}\left[h_2 K_2 x^{*2}_{\mathrm{A}_1} + h_{\mathrm{A}} K_2 K_3 x^{*3}_{\mathrm{A}_1}(2-z^*)/\right. \\ & \left.(1-z^*)^2 + h_{\mathrm{A}} K_2 K_3 K^2 \theta x^{*5}_{\mathrm{A}_1}/(1-z^*)\right]/S^* \end{aligned} \tag{17}$$

$$\begin{aligned} h^{\mathrm{E}}_{\mathrm{phys}} &= \frac{\partial\left(g^{\mathrm{E}}_{\mathrm{phys}}/T\right)}{\partial(1/T)} \\ &= R x_{\mathrm{A}} x_{\mathrm{B}} \left\{ \frac{G_{\mathrm{BA}}}{\left(x_{\mathrm{A}} + x_{\mathrm{B}} G_{\mathrm{BA}}\right)} \frac{\partial \tau_{\mathrm{BA}}}{\partial(1/T)} + \frac{G_{\mathrm{AB}}}{\left(x_{\mathrm{B}} + x_{\mathrm{A}} G_{\mathrm{AB}}\right)} \frac{\partial \tau_{\mathrm{AB}}}{\partial(1/T)} \right. \\ & \left. - \alpha_{\mathrm{AB}} \left[\frac{x_{\mathrm{A}} \tau_{\mathrm{BA}} G_{\mathrm{BA}}}{\left(x_{\mathrm{A}} + x_{\mathrm{B}} G_{\mathrm{BA}}\right)^2} \frac{\partial \tau_{\mathrm{BA}}}{\partial(1/T)} + \frac{x_{\mathrm{B}} \tau_{\mathrm{AB}} G_{\mathrm{AB}}}{\left(x_{\mathrm{B}} + x_{\mathrm{A}} G_{\mathrm{AB}}\right)^2} \frac{\partial \tau_{\mathrm{AB}}}{\partial(1/T)} \right] \right\} \end{aligned} \tag{18}$$

where S^* is the value of S at pure alcohol state and it is expressed as

$$\begin{aligned} S^* = {} & x^*_{\mathrm{A}_1} + 2K_2 x^{*2}_{\mathrm{A}_1} + K_2 K_3 x^{*3}_{\mathrm{A}_1}(3-2z^*)/(1-z^*)^2 \\ & + K_2 K_3 K^2 \theta x^{*5}_{\mathrm{A}_1}/(1-z^*) \end{aligned} \tag{19}$$

The energy parameters are assumed to be linearly temperature dependent.

$$\begin{aligned} a_{\mathrm{BA}} &= C_{\mathrm{A}} + D_{\mathrm{A}}(T - 273.15) \\ a_{\mathrm{AB}} &= C_{\mathrm{B}} + D_{\mathrm{B}}(T - 273.15) \end{aligned} \tag{20}$$

The infrared spectroscopic data [6–8] provide a fraction of the number of free hydroxyl groups in the stoichiometric number of alcohol molecules, β.

$$\begin{aligned} \beta &= \frac{\sum\limits_{i=1}^{\infty} x_{\mathrm{A}_i}(\text{open})}{\sum\limits_{i=1}^{\infty} i x_{\mathrm{A}_i}(\text{open}) + \sum\limits_{i=5}^{\infty} i x_{\mathrm{A}_i}(\text{cyclic})} \\ &= \frac{x_{\mathrm{A}_1} + K_2 x^2_{\mathrm{A}_1} + K_2 K_3 x^3_{\mathrm{A}_1}/(1-z)}{x_{\mathrm{A}_1} + 2K_2 x^2_{\mathrm{A}_1} + \left(K_2 K_3/K^3\right) z^3\left[(3-2z)/(1-z)^2 + \theta z^2/(1-z)\right]} \end{aligned} \tag{21}$$

PARAMETER DETERMINATION

An optimum set of the four equilibrium association constants was selected which reproduce the spectroscopic data and the thermodynamic properties of binary solutions of butanols in hydrocarbons over the whole composition range as well as possible. The values of K_2, K_3, K and θ which best reproduce the spectroscopic data, the activity coefficients and enthalpies of mixing in dilute solutions of alcohol are usually not suitable for the whole

TABLE 1

Association constants for butanols at 25 °C

Alcohol	K_2	K_3	K	θ
1-Butanol	30	90	35	75
2-Butanol	25	60	30	65
2-Methyl-1-propanol	30	85	30	70
2-Methyl-2-propanol	20	40	30	55

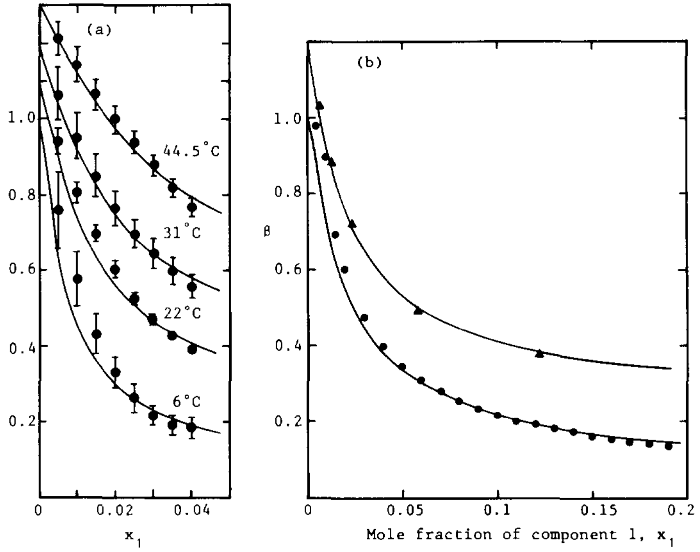

Fig. 1. Infrared spectroscopic data for fraction of free OH group for (a) 1-butanol (1) + n-heptane (2) and (b) 1-butanol (1) + n-decane (2) and 2-methyl-2-propanol (1) + cyclohexane (2). Calculated (———). Experimental: (a) (●), data of Verrall et al. [6]. Note that the ordinates for 22, 31 and 44.5 °C curves are displaced upwards by 0.1, 0.2 and 0.3, respectively, to avoid overlap and the bars indicate the average relative standard deviations: 1.34 at 6 °C; 0.38 at 22 °C; 0.90 at 31 °C; 0.50 at 44.5 °C. (b) (●), data of Fletcher and Heller [7] for 1-butanol (1) + n-decane (2) at 30 °C; (▲), data of Hoffmann [8] for 2-methyl-2-propanol (1) + cyclohexane (2) at 21.5 °C. Note that the ordinate for 2-methyl-2-propanol + cyclohexane is displaced upwards by 0.2.

concentration range. For the enthalpies of hydrogen bond formation we fixed $h_2 = -21.2$ kJ mol^{-1} and $h_A = -23.5$ kJ mol^{-1} [1], which are equivalent to those for methanol [2], ethanol [3] and propanols [4], and assumed that all h values are independent of temperature. Table 1 presents the values of K_2, K_3, K and θ for butanols and Fig. 1 shows that the model reproduces quite well the infrared data for the 1-butanol + n-heptane [6], 1-butanol + n-decane [7] and 2-methyl-2-propanol + cyclohexane [8] systems.

Binary vapor–liquid equilibrium (VLE) data were reduced from the thermodynamic relation

$$\phi_I y_I P = \gamma_I x_I \phi_I^s P_I^s \exp\left[v_I^L (P - P_I^s)/RT \right] \tag{22}$$

where y_I is the vapor-phase mole fraction of component I, P is the total pressure, P_I^s is the pure-component vapor pressure and v_I^L is the pure-liquid molar volume. P_I^s is taken from original references of VLE or calculated from the Antoine equation whose constants are available [9]. v_I^L is estimated from the modified Rackett equation [10]. The fugacity coefficients, ϕ_I and ϕ_I^s, are calculated using eqn. (23).

$$\ln \phi_I = \left(2 \sum_J y_J B_{IJ} - \sum_I \sum_J y_I y_J B_{IJ} \right) \frac{P}{RT} \tag{23}$$

where the second virial coefficients B_{IJ} are obtained from the correlation of Hayden and O'Connell [11] with the related parameters tabulated by Prausnitz et al. [12].

Parameter estimation programs were based on the simplex method [13].

CALCULATED RESULTS

Table 2 lists the values of the solvation constants and enthalpies of complex formation between butanols and aromatic hydrocarbons. Table 3 gives calculated results obtained in fitting the model to VLE data for many

TABLE 2

Solvation constants and enthalpies of complex formation at 25 °C

System (A + B)	K_{AB}	$-h_{AB}$ (kJ mol^{-1})
1-Butanol + benzene	2.8	8.2
1-Butanol + toluene	2.8	8.3
2-Butanol + benzene	2.0	8.2
2-Butanol + toluene	2.0	8.3
2-Methyl-1-propanol + benzene	2.3	8.2
2-Methyl-1-propanol + toluene	2.3	8.3
2-Methyl-2-propanol + benzene	1.8	8.2
2-Methyl-2-propanol + toluene	1.8	8.3

TABLE 3

Results of binary vapor–liquid equilibrium data reduction

System (A + B)	Temp. (°C)	No. of data points	Parameters (K)		Abs. arith. mean deviations		Ref.
			a_{BA}	a_{AB}	$10^3\Delta y$	ΔP (kPa)	
1-Butanol + cyclohexane	45	43	585.76	−364.45		0.27	14
	50	14	681.24	−410.16	9.1	0.28	15
1-Butanol + n-hexane	59.38	24	499.25	−308.20	3.2	0.61	16
1-Butanol + n-heptane	60	19	245.95	−175.48	3.8	0.19	17
	90	22	246.07	−175.36	5.5	0.36	17
1-Butanol + benzene	45	9	−251.12	320.77	3.7	0.49	18
1-Butanol + toluene	60.16	15	153.26	−109.13	9.0	0.29	19
	70.25	15	241.59	−159.54	6.1	0.13	19
	80.29	15	221.51	−141.60	5.0	0.16	19
2-Butanol + cyclohexane	45	42	397.22	−331.07		0.29	14
2-Butanol + benzene	45	10	205.67	−215.30	5.4	0.27	18
2-Butanol + toluene	60.16	13	268.34	−240.62	5.3	0.19	19
	70.25	13	269.54	−239.27	5.5	0.19	19
	80.29	12	269.44	−239.25	6.9	0.32	19
2-Methyl-1-propanol + n-hexane	59.38	13	255.66	−194.76	3.1	0.41	16
2-Methyl-1-propanol + n-heptane	60	16	247.17	−173.78	2.5	0.08	17
2-Methyl-1-propanol + benzene	45	10	264.17	−203.09	2.8	0.23	18
2-Methyl-1-propanol + toluene	60.16	15	256.95	−171.85	4.2	0.11	19
	70.25	15	258.15	−170.50	3.2	0.15	19
	80.29	15	255.50	−171.64	2.5	0.23	19
2-Methyl-2-propanol + cyclohexane	45	45	−331.14	299.76		0.21	14
	55	15	−209.90	122.60	8.8	0.47	20
2-Methyl-2-propanol + n-hexane	40	14	−310.05	283.77	7.9	0.27	21
2-Methyl-2-propanol + n-heptane	40	13	−287.72	276.32	6.8	0.08	21
2-Methyl-2-propanol + n-octane	40	13	−267.06	269.44	4.8	0.02	21
2-Methyl-2-propanol + benzene	45	11	−212.98	148.85	7.4	0.25	18
2-Methyl-2-propanol + toluene	60.16	11	−193.40	147.65	7.8	0.21	19
	70.25	14	−184.90	144.73	4.1	0.33	19
	80.29	14	−183.40	144.40	3.4	0.68	19

binary mixtures. Figures 2–5 show some representative examples. In Figs. 2 and 3 the abscissa $\sqrt{x_1}$ was used to show the quality of fit in the region up to $x_1 = 0.01$.

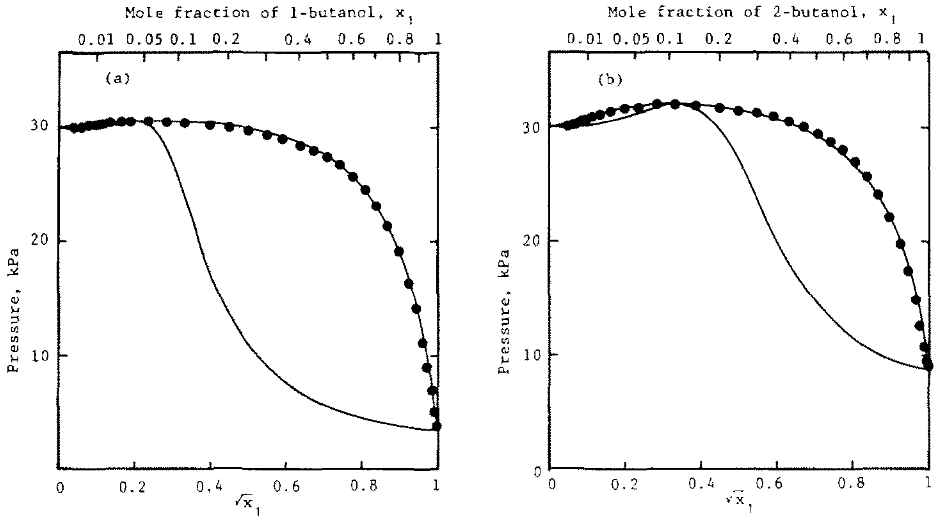

Fig. 2. Vapor–liquid equilibria for (a) 1-butanol (1) + cyclohexane (2) and (b) 2-butanol (1) + cyclohexane (2) at 45 °C. Calculated (———). Experimental (●), data of French [14].

Experimental second virial coefficients for butanols [22,23] have been reported at rather higher temperatures than those for VLE data studied here, as shown in Table 4. The Hayden–O'Connell correlation provides smaller deviations between calculated results and experimental values for 1-butanol and 2-butanol than the Tsonopoulos correlation [24] and the latter works better for 2-methyl-1-propanol and 2-methyl-2-propanol. So Smith and Srivastava [25] chose the Hayden–O'Connell correlation for 1-butanol and 2-butanol and the Tsonopoulos correlation for 2-methyl-1-propanol and

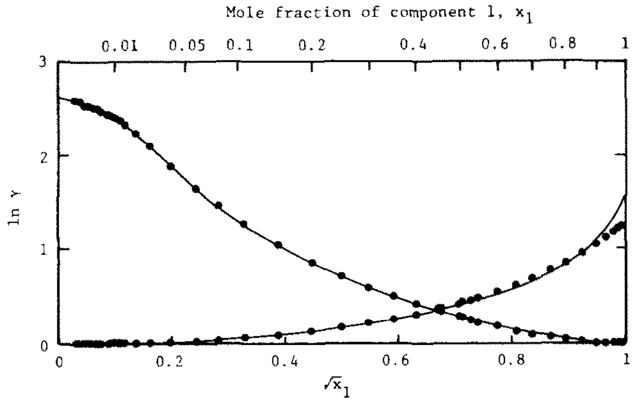

Fig. 3. Activity coefficients for 2-methyl-2-propanol (1) + cyclohexane (2) at 45 °C. Calculated (———). Experimental (●), data of French [14].

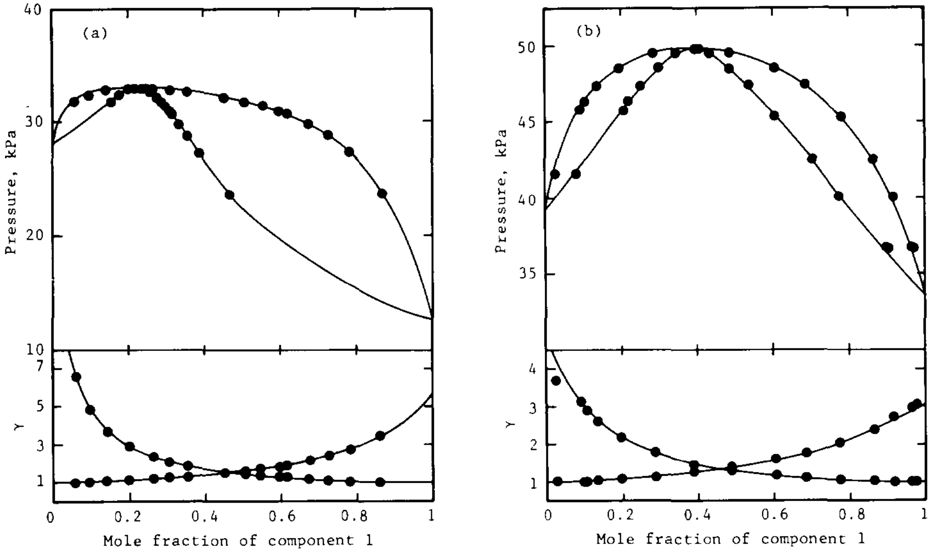

Fig. 4. Vapor–liquid equilibria for (a) 2-methyl-1-propanol (1) + n-heptane (2) at 60 °C and (b) 2-methyl-1-propanol (1) + toluene (2) at 80.29 °C. Calculated (———). Experimental (●), (a) data of Berro and Peneloux [17] and (b) data of Lnenickova and Wichterle [19].

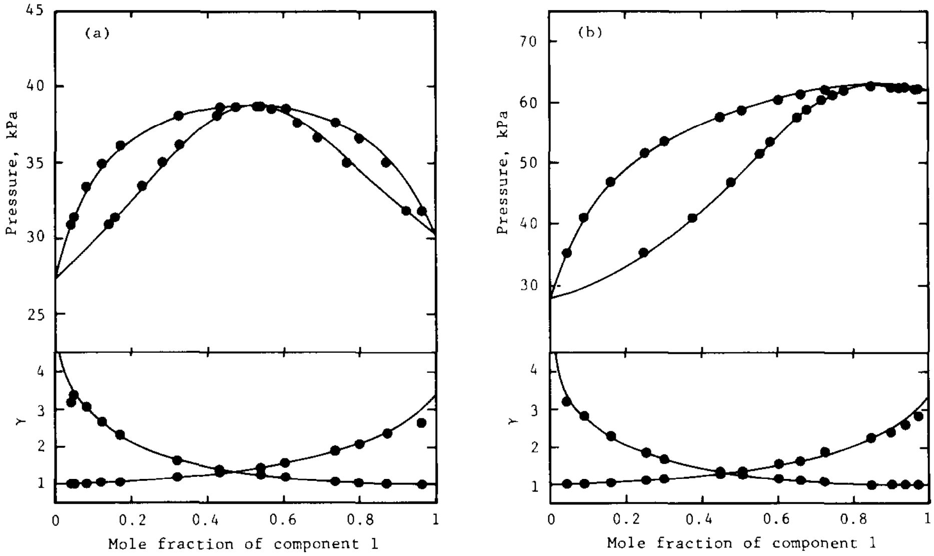

Fig. 5. Vapor–liquid equilibria for (a) 2-butanol (1) + toluene (2) and (b) 2-methyl-propanol (1) + toluene (2) at 70.25 °C. Calculated (———). Experimental (●), data of Lnenickova and Wichterle [19].

TABLE 4

Calculated results of second virial coefficients for butanols

Component	No. of data points	Temp. (°C)	Absolute arith. mean dev. (10^{-6} m^3 mol^{-1})		Reference
			I [a]	II [b]	
1-Butanol	7	77–166	36.4	80.1	22, 23
2-Butanol	4	120–166	12.0	14.5	23
2-Methyl-1-propanol	4	105–150	41.8	21.0	23
2-Methyl-2-propanol	4	105–150	66.5	29.0	23

[a] I = Hayden–O'Connell correlation.
[b] II = Tsonopoulos correlation.

TABLE 5

Comparison of vapor–liquid equilibrium data reduction based on two correlations of second virial coefficient

System (A + B)	Temp. (°C)	Type of method	Second virial coeffs. (10^{-6} m^3 mol^{-1})			Abs. arith. mean deviations	
			B_{AA}	B_{AB}	B_{BB}	$10^3\,\Delta y$	ΔP (kPa)
2-Methyl-1-propanol	59.38	I [a]	−2483	−1017	−1399	3.1	0.41
+ n-hexane		II [b]	−2669	−966	−1414	3.0	0.43
2-Methyl-2-propanol	40	I	−1728	−1168	−1654	7.9	0.27
+ n-hexane		II	−2529	−1032	−1685	8.1	0.28

[a] I = Hayden–O'Connell correlation.
[b] II = Tsonopoulos correlation.

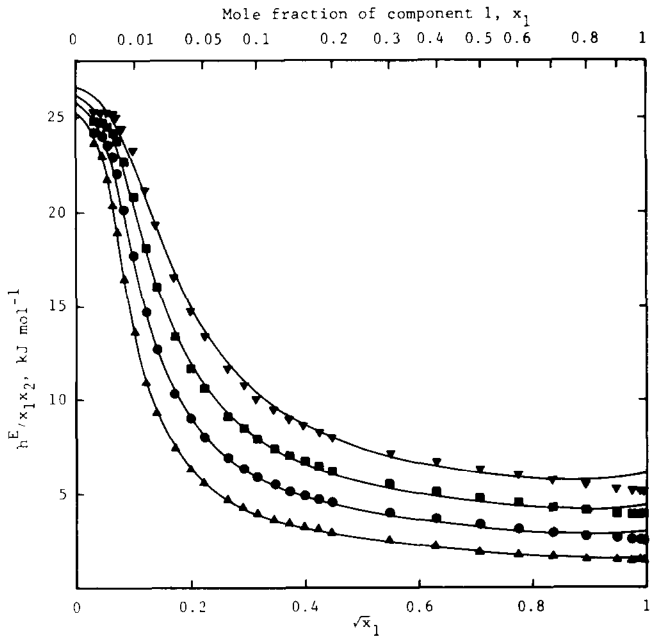

Fig. 6. Excess molar enthalpies for 1-butanol (1) + cyclohexane (2). Calculated (———). Experimental (▲, 15 °C; ●, 25 °C; ■, 35 °C; ▼, 45 °C), data of French [14].

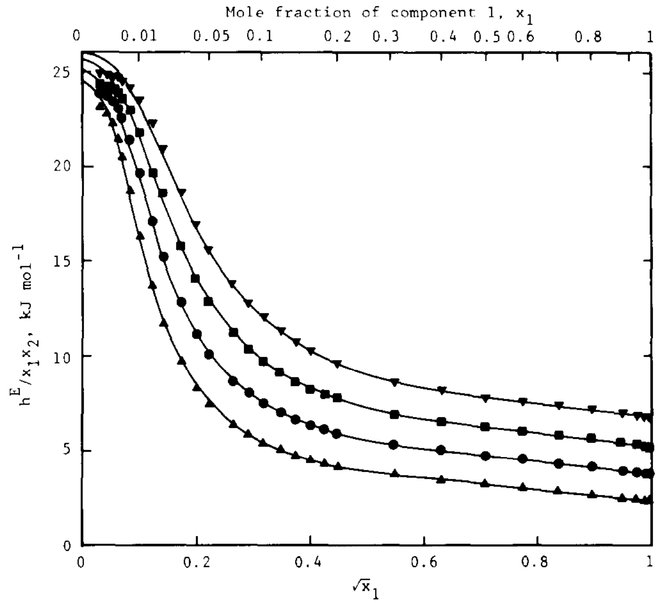

Fig. 7. Excess molar enthalpies for 2-butanol (1)+cyclohexane (2). Calculated (———). Experimental (▲, 15 °C; ●, 25 °C; ■, 35 °C; ▼, 45 °C), data of French [14].

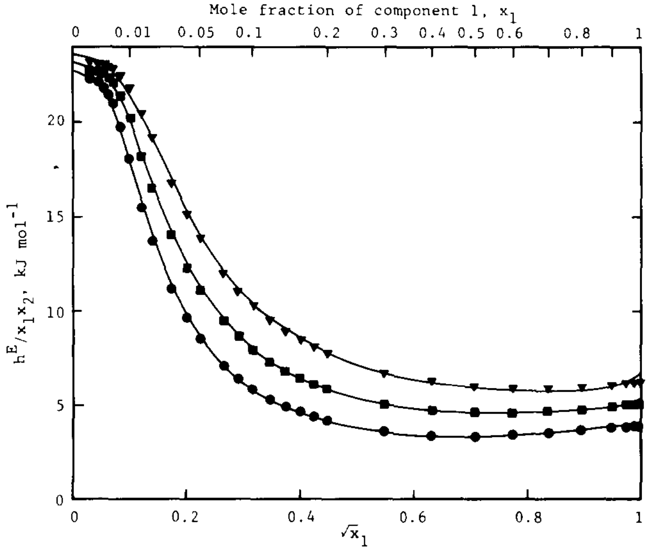

Fig. 8. Excess molar enthalpies for 2-methyl-2-propanol (1)+cyclohexane (2). Calculated (———). Experimental (●, 26 °C; ■, 35 °C; ▼, 45 °C), data of French [14].

TABLE 6

Results of binary excess molar enthalpy data reduction

System (A + B)	Temp. (°C)	No. of data points	Parameters				Abs. arith. mean dev. (J mol^{-1})	Ref.
			C_A (K)	C_B (K)	D_A	D_B		
1-Butanol + cyclohexane	15	30	3574.73	−436.85	12.5836	−1.8065	8.5 [a]	14
	25	26	−745.69	295.64	−2.3974	−0.0606	7.7	26
	25	30	1877.97	−3015.05	7.5531	−11.0509	11.8 [a]	14
	35	30	1721.82	−2831.00	6.4339	−10.3725	17.6 [a]	14
	45	30	1374.04	−2639.18	4.9094	−9.6672	17.7 [a]	14
1-Butanol + n-heptane	25	10	−837.31	869.47	−3.2038	4.1506	8.7	27
	45	10	−1259.24	986.34	−4.6662	4.7285	5.9	27
1-Butanol + benzene	25	10	−701.46	462.38	−1.1131	−1.9385	7.1	28
2-Butanol + cyclohexane	15	30	−217.41	857.38	−1.4640	3.8820	7.4 [a]	14
	25	30	−357.79	949.71	−1.8527	4.3917	7.4 [a]	14
	35	30	−789.83	585.66	−1.8032	−2.5396	6.8 [a]	14
	45	30	−928.23	601.04	−2.8039	−0.9638	5.9 [a]	14
2-Butanol + n-hexane	25	14	166.18	739.47	0.0583	2.2744	5.6	29
	45	10	2580.15	−192.00	7.8915	−1.3199	9.4	29
2-Butanol + benzene	25	8	1011.14	−696.43	5.4876	−3.0670	9.6	29
	35	8	1020.84	−631.13	5.1885	−2.7242	10.1	29
	45	8	−842.36	1471.83	−3.1421	7.8699	11.5	29

2-Methyl-1-propanol								
+ n-hexane	25	14	−698.90	222.80	−2.2029	−0.2515	9.0	29
	45	12	−277.06	366.89	−1.8912	3.3043	13.4	29
2-Methyl-1-propanol								
+ benzene	25	8	−32.04	928.99	−0.4797	5.0373	5.3	29
	35	8	20.95	1049.27	−0.1119	5.7185	3.3	29
	45	8	−224.60	528.20	−1.4756	4.0788	4.9	29
2-Methyl-2-propanol								
+ cyclohexane	26	30	322.02	−53.83	2.9843	−1.6141	7.6 [a]	14
	35	30	319.75	−113.92	2.9663	−1.5541	9.5 [a]	14
	45	30	447.89	−253.31	2.7247	−1.3343	12.6 [a]	14
2-Methyl-2-propanol								
+ n-hexane	27	10	82.49	377.82	0.7597	0.0092	4.1	29
	45	9	34.07	290.57	0.7290	0.1347	2.6	29
2-Methyl-2-propanol								
+ benzene	27	8	650.10	77.34	3.1948	−0.9291	7.6	29
	35	8	581.17	−299.43	4.5312	−2.1587	3.9	29
	45	8	1434.17	904.67	6.4107	2.7164	11.5	29
Benzene + cyclohexane	25	18	−46.62	−586.90	−1.4246	−2.1826	2.2	30

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[a] Fitted to h^{E}/x_1x_2.

2-methyl-2-propanol. It is to be noted that Hayden–O'Connell correlation parameters, RG, MU and ETA, which are listed in ref. 25, are misprinted. VLE data for the 2-methyl-1-propanol + n-hexane and 2-methyl-2-propanol + n-hexane systems were also reduced using a set of second virial coefficients derived from the Tsonopoulos correlation. Table 5 indicates that the results of VLE data reduction for these two systems are nearly the same regardless of different sets of second virial coefficients.

Table 6 presents calculated results of binary excess molar enthalpy data reduction. Figures 6–8 compare the calculated values with the experimental results of h^E/x_1x_2 of solutions of butanols with cyclohexane [14].

The model can be extended to ternary mixtures including one alcohol and two nonassociating components by use of binary parameters without any additional ternary constants [2–4]. Isothermal ternary VLE data for mixtures of butanols with hydrocarbons were not available to us. Only one set of the excess molar enthalpy data of 1-butanol + benzene + cyclohexane at 25 °C is available [31]. The average arithmetic mean deviation between calculated and experimental values is 13.9 J mol^{-1}, showing that the agreement is acceptable.

In conclusion, the association model reproduces well the thermodynamic properties of solutions of butanols with hydrocarbons.

LIST OF SYMBOLS

A, B	alcohol and hydrocarbon
a_{IJ}	binary interaction parameter of NRTL equation
B_{IJ}	second virial coefficient
C_I, D_I	coefficients of eqn. (20)
G_{IJ}	coefficient as defined by $\exp(-\alpha_{IJ}\tau_{IJ})$
g^E	excess molar Gibbs free energy
h_2	enthalpy of hydrogen bond formation of dimer
h_A	enthalpy of hydrogen bond formation for all $i > 2$, including cyclic case
h_{AB}	enthalpy of formation of chemical complex A_iB
h^E	excess molar enthalpy
K_2	equilibrium association constant for formation of dimer
K_3	equilibrium association constant for formation of open trimer
K	equilibrium association constant for formation of open-chain i-mer, $i > 3$
K_{cy}	equilibrium association constant for cyclization of open-chain i-mer as defined by θ/i, $i > 4$
K_{AB}	equilibrium solvation constant for formation of chemical complex A_iB
P	total pressure

P_I^{s}	saturated vapor pressure of pure component I
R	universal gas constant
S	stoichiometric sum
T	absolute temperature
v_I^{L}	liquid molar volume of pure component I
x_I	liquid-phase mole fraction of component I
y_I	vapor-phase mole fraction of component I
z	coefficient as defined by Kx_{A_1}

Greek letters

α_{IJ}	nonrandomness parameter of NRTL equation taken as 0.3, $\alpha_{IJ} = \alpha_{JI}$
β	coefficient as defined by eqn. (21)
γ_I	activity coefficient of component I
θ	constant related to K_{cy}
τ_{IJ}	coefficient as defined by a_{IJ}/T
ϕ_I	vapor-phase fugacity coefficient of component I
ϕ_I^{s}	vapor-phase fugacity coefficient of pure component I at system temperature T and pressure P

Subscripts

A, B	alcohol and hydrocarbon
A_1, A_i	alcohol monomer and i-mer
AB	complex formation between alcohol open-chain i-mer and component B
$\mathrm{A}_i\mathrm{B}$	complex formed by alcohol open-chain i-mer and component B
chem	chemical
I, J	components I and J
phys	physical

Superscripts

E	excess
L	liquid
s	saturation
*	pure-alcohol reference state

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