Thermochimica Acta, 87 (1985) 129–140
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMODYNAMICS OF SOLUTIONS OF PROPANOLS IN NONASSOCIATING COMPONENTS

ISAMU NAGATA * and KAZUHIRO TAMURA

Department of Chemical Engineering, Kanazawa University, 2-40-20, Kodatsuno, Kanazawa 920 (Japan)

(Received 12 November 1984)

ABSTRACT

The spectroscopic and thermodynamic properties of solutions of propanols in various nonassociating components can be described well by an associated solution model in which the association of alcohol molecules into open-chain and cyclic hydrogen-bonded species and the formation of complexes between the terminal hydroxyl group of the alcohol chain molecules and a solvating component are taken into account, with allowance for a non-polar interaction term. Ternary predicted values of vapor–liquid equilibria and excess enthalpies for mixtures including propanol and two nonassociating components are in good agreement with experimental results.

INTRODUCTION

The properties of alcohol solutions have been studied by many investigators who used chemical association models. Chemical models have some advantages over physical models, because the extremely nonideal behavior of the alcohol solutions can be explained by introducing equilibrium constants. Recently, we [1,2] presented a chemical model which can account for the infrared spectroscopic change in the dilute solution of alcohol, the activity coefficients of the alcohol and nonassociating components, the excess enthalpies over the whole composition range and the occurrence of phase separation. In this paper the new model is further extended to the spectroscopic property, isothermal vapor–liquid equilibrium and excess enthalpy data of solutions of propanols with nonassociated components.

---

* Author to whom correspondence should be addressed.

THEORY

The model we have selected is one which has been used for the systems methanol– and ethanol–nonassociating component [1,2]. The model assumes that linear chain species of alcohol of any length as well as closed cyclic species are present, the smallest cyclic alcohol being a pentamer, and further that linear polymeric complexes are formed between the terminal hydroxyl group of alcohol chain species and an active nonassociating component. The NRTL equation [3] has been allowed as a physical interaction term for non-polar interaction.

The enthalpies of hydrogen-bond formation in the alcohol dimer and higher polymers are h_2 and h_A, which are assumed temperature-independent. The equilibrium constants for the linear and cyclic alcohol polymer formation are expressed by K_2 for $A + A = A_2$, K_3 for $A_2 + A = A_3$, K for all linear polymerization $A_i + A = A_{i+1}$, where $i \geq 3$, and $K_{cy} = \theta/i$ for $A_i(\text{open}) = A_i(\text{cyclic})$, where θ is independent of i and $i > 4$. The solvation equilibrium constants between unlike molecules are given by K_{AB} for $A_i + B = A_iB$, K_{AC} for $A_i + C = A_iC$ and K_{BC} for $B + C = BC$.

The activity coefficients of all components in a ternary mixture composed of the alcohol (A) and two nonassociating components (B and C) are given as the sum of the chemical and physical contribution terms. These two terms are expressed by

$$(\ln \gamma_A)_{chem} = \ln(x_{A_1}/x^*_{A_1}x_A) \tag{1}$$

$$(\ln \gamma_B)_{chem} = \ln(x_{B_1}/x_B) \tag{2}$$

$$(\ln \gamma_C)_{chem} = \ln(x_{C_1}/x_C) \tag{3}$$

$$(\ln \gamma_I)_{phys} = \frac{\sum\limits_J \tau_{JI} G_{JI} x_J}{\sum\limits_K G_{KI} x_K} + \sum_J \frac{\sum\limits_J x_J G_{IJ}}{\sum\limits_K G_{KJ} x_K} \left(\tau_{IJ} - \frac{\sum\limits_R x_R \tau_{RJ} G_{RJ}}{\sum\limits_K G_{KJ} x_K} \right) \tag{4}$$

where

$$\tau_{JI} = (g_{JI} - g_{II})/RT \tag{5}$$

$$G_{JI} = \exp(-\alpha_{JI}\tau_{JI}) \tag{6}$$

where the nonrandomness parameter $\alpha_{JI}(=\alpha_{IJ})$ is taken as 0.3 and the binary parameters, $g_{JI} - g_{II}$ and $g_{IJ} - g_{JJ}$, are obtained from experimental phase equilibrium data.

The monomer mole fractions as the three components are related to the overall mole fractions of the components.

$$x_A = \Big\{ (1 + K_{AB}x_{B_1} + K_{AC}x_{C_1}) \left[x_{A_1} + 2K_2 x_{A_1}^2 + K_2K_3x_{A_1}^3(3 - 2z)/(1 - z)^2 \right] + K_2K_3K^2\theta x_{A_1}^5/(1 - z) \Big\} / S \tag{7}$$

$$x_{\mathrm{B}} = \left\{x_{\mathrm{B}_1} + K_{\mathrm{BC}} x_{\mathrm{B}_1} x_{\mathrm{C}_1} + K_{\mathrm{AB}} x_{\mathrm{B}_1}\left[x_{\mathrm{A}_1} + K_2 x_{\mathrm{A}_1}^2 + K_2 K_3 x_{\mathrm{A}_1}^3/(1-z)\right]\right\}/S \tag{8}$$

$$x_{\mathrm{C}} = \left\{x_{\mathrm{C}_1} + K_{\mathrm{BC}} x_{\mathrm{B}_1} x_{\mathrm{C}_1} + K_{\mathrm{AC}} x_{\mathrm{C}_1}\left[x_{\mathrm{A}_1} + K_2 x_{\mathrm{A}_1}^2 + K_2 K_3 x_{\mathrm{A}_1}^3/(1-z)\right]\right\}/S \tag{9}$$

where $z = K x_{\mathrm{A}_1}$ and S is the stoichiometric sum given by

$$\begin{aligned} S = {} & \left(1 + K_{\mathrm{AB}} x_{\mathrm{B}_1} + K_{\mathrm{AC}} x_{\mathrm{C}_1}\right)\left[x_{\mathrm{A}_1} + 2K_2 x_{\mathrm{A}_1}^2 + K_2 K_3 x_{\mathrm{A}_1}^3 (3-2z)/(1-z)^2\right] \\ & + K_2 K_3 K^2 \theta x_{\mathrm{A}_1}^5/(1-z) + \left(K_{\mathrm{AB}} x_{\mathrm{B}_1} + K_{\mathrm{AC}} x_{\mathrm{C}_1}\right)\left[x_{\mathrm{A}_1} + K_2 x_{\mathrm{A}_1}^2\right. \\ & \left. + K_2 K_3 x_{\mathrm{A}_1}^3/(1-z)\right] + 2K_{\mathrm{BC}} x_{\mathrm{B}_1} x_{\mathrm{C}_1} + x_{\mathrm{B}_1} + x_{\mathrm{C}_1} \end{aligned} \tag{10}$$

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

$$\begin{aligned} & \sum_{i=1}^{\infty} x_{\mathrm{A}_i}(\text{linear}) + \sum_{i=1}^{\infty} x_{\mathrm{A}_i\mathrm{B}_1} + \sum_{i=1}^{\infty} x_{\mathrm{A}_i\mathrm{C}_1} + \sum_{i=5}^{\infty} x_{\mathrm{A}_i}(\text{cyclic}) + x_{\mathrm{B}_1\mathrm{C}_1} + x_{\mathrm{B}_1} + x_{\mathrm{C}_1} \\ & = \left(1 + K_{\mathrm{AB}} x_{\mathrm{B}_1} + K_{\mathrm{AC}} x_{\mathrm{C}_1}\right)\left[x_{\mathrm{A}_1} + K_2 x_{\mathrm{A}_1}^2 + K_2 K_3 x_{\mathrm{A}_1}^3/(1-z)\right] \\ & - \left(K_2 K_3 \theta/K^3\right)\left[\ln(1-z) + z + z^2/2 + z^3/3 + z^4/4\right] \\ & + K_{\mathrm{BC}} x_{\mathrm{B}_1} x_{\mathrm{C}_1} + x_{\mathrm{B}_1} + x_{\mathrm{C}_1} = 1 \end{aligned} \tag{11}$$

These mass balance equations can be solved for x_{A_1}, x_{B_1} and x_{C_1} at any composition.

At pure alcohol state eqn. (11) reduces to

$$\begin{aligned} & \sum_{i=1}^{\infty} x^*_{\mathrm{A}_i}(\text{linear}) + \sum_{i=5}^{\infty} x^*_{\mathrm{A}_i}(\text{cyclic}) \\ & = x^*_{\mathrm{A}_1} + K_2 x^{*2}_{\mathrm{A}_1} + K_2 K_3 x^{*3}_{\mathrm{A}_1}/(1-z^*) \\ & \quad - \left(K_2 K_3 \theta/K^3\right)\left[\ln(1-z^*) + z^* + z^{*2}/2 + z^{*3}/3 + z^{*4}/4\right] = 1 \end{aligned} \tag{12}$$

Equation (12) can be solved for $x^*_{\mathrm{A}_1}$.

The excess molar enthalpy of the ternary mixture is expressed by the sum of chemical and physical terms.

$$\begin{aligned} h^{\mathrm{E}}_{\mathrm{chem}} = {} & \left\{\left(1 + K_{\mathrm{AB}} x_{\mathrm{B}_1} + K_{\mathrm{AC}} x_{\mathrm{C}_1}\right)\left[h_2 K_2 x_{\mathrm{A}_1}^2 + h_{\mathrm{A}} K_2 K_3 x_{\mathrm{A}_1}^3 (2-z)/(1-z)^2\right]\right. \\ & + h_{\mathrm{A}} K_2 K_3 K^2 \theta x_{\mathrm{A}_1}^5/(1-z) + \left(h_{\mathrm{AB}} K_{\mathrm{AB}} x_{\mathrm{B}_1} + h_{\mathrm{AC}} K_{\mathrm{AC}} x_{\mathrm{C}_1}\right) \\ & \left. \times \left[x_{\mathrm{A}_1} + K_2 x_{\mathrm{A}_1}^2 + K_2 K_3 x_{\mathrm{A}_1}^3/(1-z)\right] + h_{\mathrm{BC}} K_{\mathrm{BC}} x_{\mathrm{B}_1} x_{\mathrm{C}_1}\right\}/S \\ & - x_{\mathrm{A}}\left[h_2 K_2 x^{*2}_{\mathrm{A}_1} + h_{\mathrm{A}} K_2 K_3 x^{*3}_{\mathrm{A}_1}(2-z^*)/(1-z^*)^2\right. \\ & \left. + h_{\mathrm{A}} K_2 K_3 K^2 \theta x^{*5}_{\mathrm{A}_1}/(1-z^*)\right]/S^* \end{aligned} \tag{13}$$

where S^* is the value of S at pure alcohol state.

$$\begin{aligned} S^* = {} & x^*_{\mathrm{A}_1} + 2K_2 x^{*2}_{\mathrm{A}_1} + K_2 K_3 x^{*3}_{\mathrm{A}_1}(3-2z^*)/(1-z^*)^2 \\ & + K_2 K_3 K^2 \theta x^{*5}_{\mathrm{A}_1}/(1-z^*) \end{aligned} \tag{14}$$

$$h^{\mathrm{E}}_{\mathrm{phys}} = R\sum_I x_I \left[\frac{\sum_J x_J \dfrac{\partial(\tau_{JI}G_{JI})}{\partial(1/T)}}{\sum_K G_{KI}x_K} - \frac{\sum_J \tau_{JI}G_{JI}x_J \sum_K x_K \dfrac{\partial G_{KI}}{\partial(1/T)}}{\left(\sum_K G_{KI}x_K\right)^2} \right] \tag{15}$$

and the temperature dependency of the energy parameter is given by

$$g_{JI} - g_{II} = C_I + D_I(T - 273.15) \tag{16}$$

The infrared spectroscopic data provide a fraction of the number of free hydroxyl groups in the stoichiometric number of alcohol molecules, β

$$\begin{aligned}\beta &= \frac{\sum_{i=1}^{\infty} x_{\mathrm{A}_i}(\text{linear})}{\sum_{i=1}^{\infty} i x_{\mathrm{A}_i}(\text{linear}) + \sum_{i=5}^{\infty} i x_{\mathrm{A}_i}(\text{cyclic})} \\ &= \frac{x_{\mathrm{A}_1} + K_2 x_{\mathrm{A}_1}^2 + K_2K_3x_{\mathrm{A}_1}^3/(1-z)}{x_{\mathrm{A}_1} + 2K_2x_{\mathrm{A}_1}^2 + \left(K_2K_3/K^3\right)z^3\left[(3-2z)/(1-z)^2 + \theta z^2/(1-z)\right]}\end{aligned} \tag{17}$$

CALCULATED RESULTS

Reproduction of binary experimental data

The temperature dependency of the equilibrium constants is expressed by the van’t Hoff relation.

$$\begin{aligned} &\partial \ln K_2/\partial(1/T) = -h_2/R, && \partial \ln K_3/\partial(1/T) = -(2h_{\mathrm{A}} - h_2)/R \\ &\partial \ln K/\partial(1/T) = -h_{\mathrm{A}}/R, && \partial \ln \theta/\partial(1/T) = -h_{\mathrm{A}}/R \\ &\partial \ln K_{\mathrm{AB}}/\partial(1/T) = -h_{\mathrm{AB}}/R, && \partial \ln K_{\mathrm{AC}}/\partial(1/T) = -h_{\mathrm{AC}}/R \\ &\partial \ln K_{\mathrm{BC}}/\partial(1/T) = -h_{\mathrm{BC}}/R \end{aligned} \tag{18}$$

Many combinations of K_2, K_3, K and θ were tested for reproducing the experimental thermodynamic functions of alcohol–saturated hydrocarbon mixtures with good accuracy. Finally, a good set of these equilibrium constants at 25°C was selected as follows: for 1-propanol, $K_2 = 35$, $K_3 = 90$, $K = 40$ and $\theta = 75$; for 2-propanol, $K_2 = 35$, $K_3 = 85$, $K = 30$ and $\theta = 70$. The value of h_2 is -21.2 kJ mol^{-1} and h_{A} is -23.5 kJ mol^{-1} [1,2]. Table 1 lists the values of the solvation constants and enthalpies of complex formation. The values of enthalpies of complex formation were taken from previous papers [1,2,4]. Figure 1 shows that the model fits infrared data well for the 1-propanol–*n*-heptane and 2-propanol–tetrachloromethane systems. Lien [5] made infrared spectroscopic measurements for the 1-propanol–*n*-

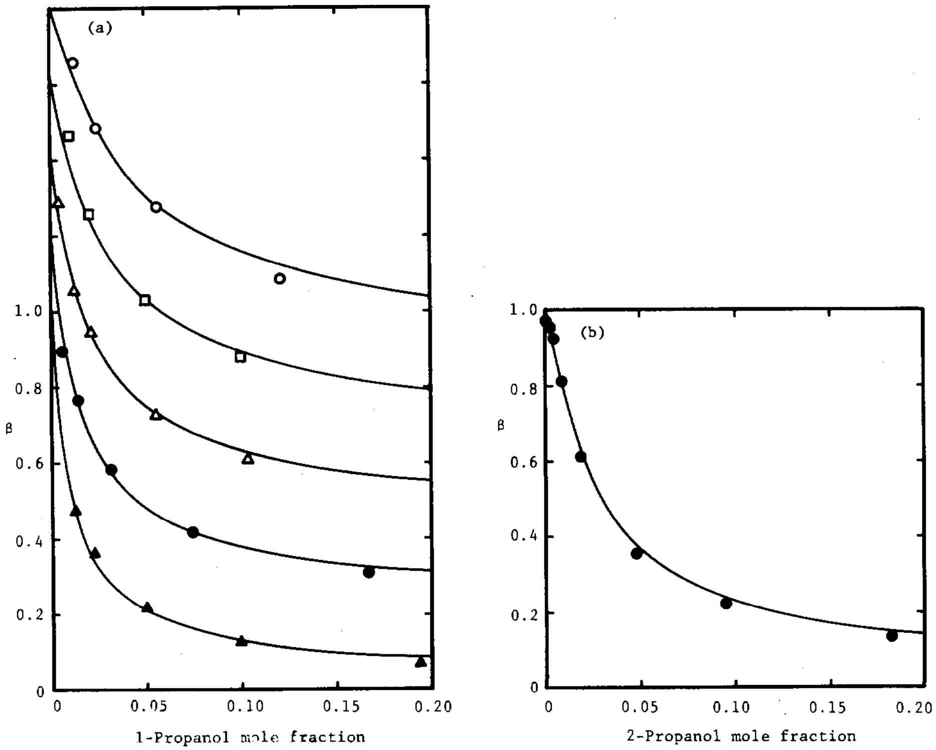

Fig. 1. Observed and calculated infrared spectroscopic data for fraction of free OH groups of propanol molecules for (a) 1-propanol–*n*-heptane and (b) 2-propanol–tetrachloromethane. Calculated (———). (a) Experimental (▲, 15°C; ●, 25°C; △, 35°C; □, 45°C; ○, 55°C), data of Lien [5]. Note that the ordinates for 25, 35, 45 and 55°C curves are replaced upwards by 0.2, 0.4, 0.6 and 0.8, respectively, to avoid overlap. (b) Experimental (●), data of Hoffmann [6] at 21.5°C.

TABLE 1

Solvation equilibrium constants and enthalpies of complex formation

System	Temp. (°C)	*K*	$-h$ (kJ mol^{-1})
1-Propanol–benzene	25	3	8.2
1-Propanol–butyl chloride	25	1.8	
1-Propanol–chloroform	55	12	24.5
1-Propanol–ethyl acetate	25	13	15
1-Propanol–*p*-xylene	25	2.5	8.3
2-Propanol–benzene	25	2.8	8.2
2-Propanol–2-butanone	50	12	
2-Propanol–chloroform	50	8	24.5
2-Propanol–ethyl acetate	25	12	15
2-Propanol–tetrachloromethane	25	0.9	5.5
2-Propanol–toluene	25	2.4	8.3
2-Propanol–*p*-xylene	25	2.3	8.3
Chloroform–benzene	26	0.36	4

heptane system and his absorbance data obtained by the subtraction method were used to derive the infrared data in Fig. 1a.

Vapor–liquid equilibrium data were reduced by using the equation

$$\phi_I y_I P = x_I \gamma_I \phi_I^s P_I^s \exp\left[v_I^L (P - P_I^s)/RT \right] \tag{19}$$

where y is the vapor mole fraction, P is the total pressure, P^s is the saturation pressure of pure component, ϕ is the fugacity coefficient obtained from the volume-explicit virial equation of state truncated after the second term and v^L is the pure liquid molar volume. The pure component vapor pressures were calculated by using the Antoine equation [7,8]. The second virial coefficients were estimated by the generalized method of Hayden and O'Connell [9].

The energy parameters were obtained by minimizing the sum-of-squares of relative deviation in pressure plus the sum-of-squares of deviations in vapor-phase mole fraction by means of the simplex method [10]. Table 2 presents binary results of vapor–liquid equilibrium data reduction and Figs. 2 and 3 give typical examples to show the capability of the model in data reduction. Table 3 gives binary results of excess enthalpy data and Fig. 4 shows that the model is able to reproduce excess enthalpy data having endo- and exothermic regions for propanol–chloroform mixtures with sufficient accuracy.

TABLE 2

Binary results of vapor–liquid equilibrium data reduction

System (A–B)	Temp. (°C)	No. of data points	Energy parameters		Abs. arith. mean dev.		Ref.
			$g_{BA} - g_{AA}$ (J mol^{-1})	$g_{AB} - g_{BB}$ (J mol^{-1})	Vapor mole fraction ($\times 10^3$)	Press. (mmHg)	
1-Propanol–benzene	45	11	1983.40	−1456.30	7.0	2.8	11
1-Propanol–butyl chloride	25	15	2424.32	−1883.79		1.8	12
1-Propanol–chloroform	55	9	6110.96	−2933.11	5.8	1.4	13
1-Propanol–ethyl acetate	55	12	1650.76	−1237.18	8.1	2.9	14
1-Propanol–*n*-heptane	25	11	710.68	30.23		0.4	12
1-Propanol–*n*-hexane	45	5	530.15	60.30	2.2	1.0	15
2-Propanol–benzene	45	12	−739.99	1368.41	7.7	2.2	16
	50	15	−861.33	1637.21	5.4	1.8	17
2-Propanol–2-butanone	50	5	230.47	472.66	14.5	3.8	18
2-Propanol–chloroform	50	11	2299.67	−1450.17	3.0	1.2	19
2-Propanol–cyclohexane	50	11	2249.27	−1503.39	3.1	2.4	17
2-Propanol–ethyl acetate	55	12	−1158.01	1672.73	9.7	2.1	14
Benzene–cyclohexane	50	5	2138.02	−502.08	7.2	1.1	20
2-Butanone–benzene	50	5	2230.07	−1322.14	3.8	0.6	18
Butyl chloride–*n*-heptane	25	11	1071.05	71.05		0.2	12
Chloroform–benzene	50	19	−1549.19	2008.91	3.1	1.5	21

TABLE 3

Binary results of excess enthalpy data reduction at 25°C

System (A–B)	No. of data points	Abs. arith. mean dev. (J mol^{-1})	C_A (J mol^{-1})	C_B (J mol^{-1})	D_A (J mol^{-1} K^{-1})	D_B (J mol^{-1} K^{-1})	Ref.
1-Propanol–benzene	10	7.9	−9940.33	4944.27	−32.3402	16.7461	22
1-Propanol–chloroform	18	14.9	7888.27	6233.72	−6.4841	39.2615	23
1-Propanol–cyclohexane	18	3.0	2076.75	8825.71	4.4276	34.0759	24
1-Propanol–ethyl acetate	23	6.2	13272.5	2255.24	57.9231	7.6835	25
1-Propanol–*p*-xylene	16	8.8	−4301.72	4063.38	−19.6686	36.0334	26
2-Propanol–benzene	17	7.0	−9128.92	4032.49	−30.7181	6.2905	27
2-Propanol–chloroform	22	11.5	7107.90	9225.03	−5.7016	47.9968	23
2-Propanol–cyclohexane	18	9.1	−5104.25	6720.19	−22.3718	35.9533	28
2-Propanol–ethyl acetate	19	13.6	−2580.33	2670.42	−10.5771	5.4994	29
2-Propanol–toluene	10	3.6	−6462.50	4354.58	−15.5777	−9.4738	22
2-Propanol–*p*-xylene	17	2.9	−5946.40	4639.70	−10.0472	−19.0478	26
Benzene–cyclohexane	23	2.2	−387.62	−4879.50	−11.8441	−18.1458	24
Ethyl acetate–cyclohexane	15	5.7	3064.03	4049.85	−11.4516	5.5445	30
Toluene–cyclohexane	12	3.3	1127.62	−1034.15	−13.0536	1.7853	31
p-Xylene–cyclohexane	19	2.6	1609.44	−956.63	−11.8524	2.6662	26

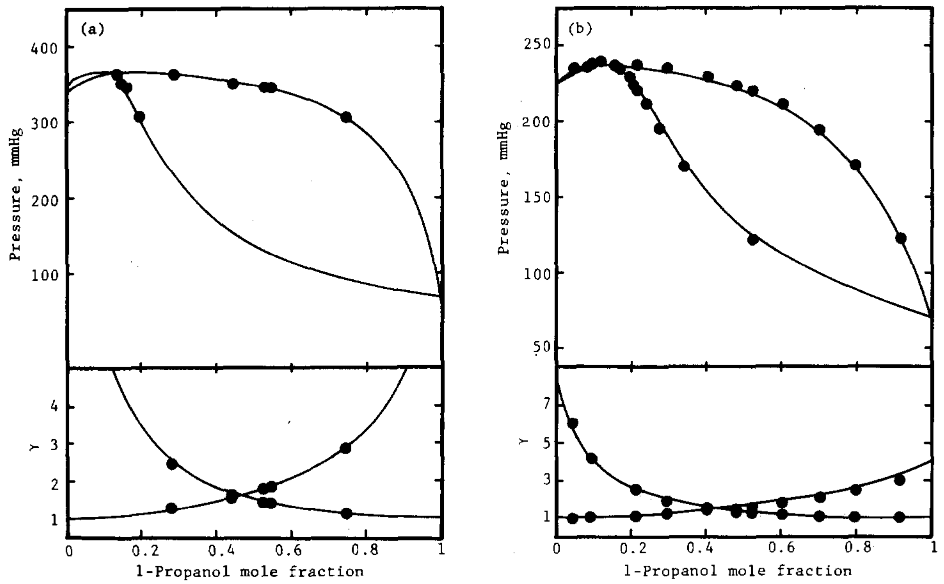

Fig. 2. Vapor–liquid equilibria for (a) 1-propanol(1)–*n*-hexane(2) and (b) 1-propanol(1)–benzene(2) at 45°C. Calculated (———). Experimental (●): (a), data of Brown et al. [15]; (b), data of Brown and Smith [11].

Ternary predictions from binary data

Tables 4 and 5 summarize vapor–liquid equilibrium and excess enthalpy predictions for several representative ternary mixtures. Agreement is accep-

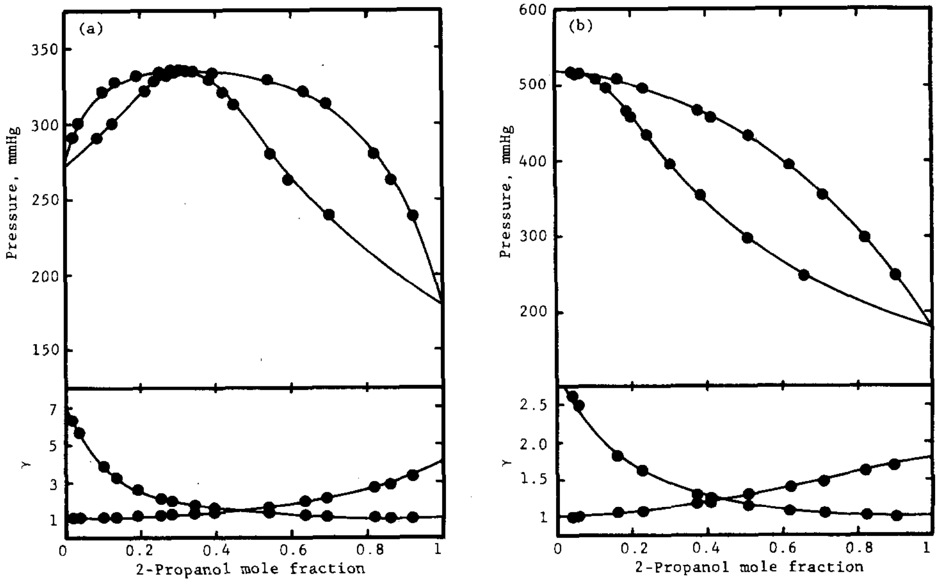

Fig. 3. Vapor–liquid equilibria for (a) 2-propanol(1)–benzene(2) and (b) 2-propanol(1)–chloroform(2) at 50°C. Calculated (———). Experimental (●): (a), data of Nagata et al. [17]; (b), data of Nagata [19].

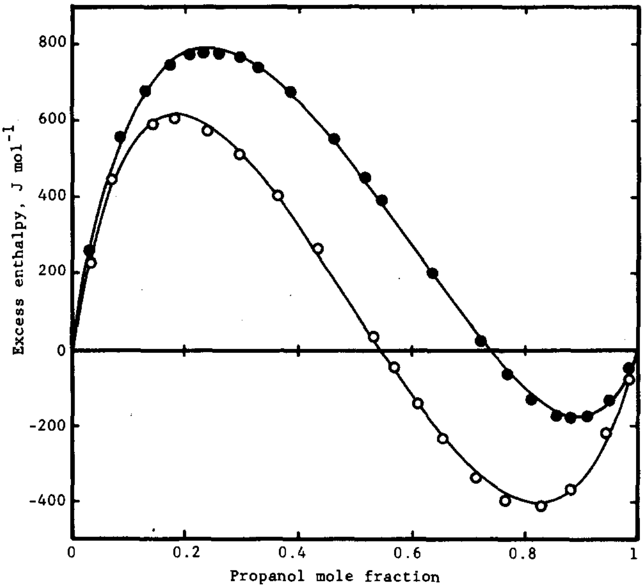

Fig. 4. Molar excess enthalpies for 1-propanol(1)–chloroform(2) and 2-propanol(1)–chloroform(2) at 25°C. Calculated (———). Experimental data of Nagata et al. [23]: (○), 1-propanol–chloroform; (●), 2-propanol–chloroform.

TABLE 4

Predicted results for ternary vapor–liquid equilibria

System	Temp. (°C)	No. of data points	Abs. arith. mean dev.		Ref.
			Vapor mole fraction ($\times 10^3$)	Pressure (mmHg)	
1-Propanol–butyl chloride–*n*-heptane	25	44		2.2	12
2-Propanol–benzene–cyclohexane	40	6	8.2 4.1 6.6	1.5	16
2-Propanol–benzene–cyclohexane	55	6	12.2 5.1 8.3	1.7	16
2-Propanol–2-butanone–benzene	50	19	9.3 11.3 4.9	1.5	18
2-Propanol–chloroform–benzene	50	16	12.9 9.0 6.5	6.6	19

TABLE 5

Predicted results for ternary excess enthalpies at 25°C

System	No. of data points	Abs. arith. mean dev. (J mol^{-1})	Ref.
1-Propanol–ethyl acetate–cyclohexane	55	26.5	32
1-Propanol–*p*-xylene–cyclohexane	42	10.9	26
2-Propanol–benzene–cyclohexane	67	16.7	28
2-Propanol–ethyl acetate–cyclohexane	57	19.4	32
2-Propanol–toluene–cyclohexane	56	11.9	33
2-Propanol–*p*-xylene–cyclohexane	55	17.9	26

table between calculated and experimental values. The calculated results indicate that the association model can be used to predict the ternary thermodynamic properties of solutions of propanols with nonassociating components from binary information alone.

NOTATION

C_I, D_I	constants of eqn. (16)
G_{IJ}	coefficients as defined by $\exp(-\alpha_{IJ}\tau_{IJ})$
g_{IJ}	binary interaction parameter
h_2	enthalpy of formation of dimer
h_A	enthalpy of hydrogen bond formation in *i*-mer
h_{AB}, h_{AC}	enthalpies of formation of chemical complexes A_iB and A_iC
h_{BC}	enthalpy of formation of chemical complex B_1C_1
h^E	excess enthalpy
K_2	equilibrium constant of dimer
K_3	equilibrium constant of open chain trimer
K	equilibrium constant of open chain *i*-mer formation, $i > 3$
K_{cy}	equilibrium constant for cyclization of open chain *i*-mer as defined by θ/i, $i > 4$
K_{AB}, K_{AC}	equilibrium constants of formation of chemical complexes A_iB and A_iC
K_{BC}	equilibrium constant of formation of chemical complex B_1C_1
P	total pressure
P_I^s	saturation pressure of pure component I
R	universal gas constant
T	absolute temperature
v_I^L	molar liquid volume of pure component I
x_I	liquid mole fraction of component I
y_I	vapor mole fraction of component I
z	coefficient as defined by Kx_{A_1}

Greek letters

α_{IJ}	nonrandomness parameter of NRTL equation
β	coefficient as defined by eqn. (17)
γ_I	activity coefficient of component I
θ	constant related to K_{cy}
τ_{JI}	coefficient as defined by $(g_{JI} - g_{II})/RT$
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_I^{s}

Subscripts

A, B, C	alcohol and nonassociating components
A_1, A_i	alcohol monomer and i-mer
$\mathrm{A}_i\mathrm{B}$, $\mathrm{A}_i\mathrm{C}$	complex formation between alcohol i-mer and components B and C
BC	1 : 1 complex between components B and C
chem	chemical
I,J,K	components
phys	physical

Superscripts

E	excess
L	liquid
s	saturation
*	pure alcohol

REFERENCES

1 I. Nagata and K. Tamura, Thermochim. Acta, 57 (1982) 331.
2 I. Nagata and K. Tamura, Thermochim. Acta, 77 (1984) 281.
3 H. Renon and J.M. Prausnitz, AIChE J., 14 (1968) 135.
4 I. Nagata, K. Tamura and S. Tokuriki, Thermochim. Acta, 47 (1981) 315.
5 T.R. Lien, Ph.D. Thesis, University of Toronto, Toronto, Ontario, 1972.
6 E.G. Hoffmann, Z. Phys. Chem. (Leipzig), 53 (1943) 179.
7 J.A. Riddick and W.B. Bunger, Organic Solvents, 3rd edn., Wiley-Interscience, New York, 1970.
8 T. Boublik, V. Fried and E. Hâla, The Vapour Pressures of Pure Substances, Elsevier, Amsterdam, 1973.
9 J.G. Hayden and J.P. O'Connell, Ind. Eng. Chem., Process Des. Dev., 14 (1975) 209.
10 J.A. Nelder and R. Mead, Comput. J., 7 (1965) 308.
11 I. Brown and F. Smith, Aust. J. Chem., 12 (1959) 407.
12 S.G. Sayegh, J.H. Vera and G.A. Ratcliff, Can. J. Chem. Eng., 57 (1979) 513.

13 I. Nagata, J. Chem. Thermodyn., 17 (1985) in press.
14 I. Nagata, T. Yamada and S. Nakagawa, J. Chem. Eng. Data, 20 (1975) 271.
15 I. Brown, W. Fock and F. Smith, J. Chem. Thermodyn., 1 (1969) 273.
16 I. Brown, W. Fock and F. Smith, Aust. J. Chem., 9 (1956) 364.
17 I. Nagata, T. Ohta and Y. Uchiyama, J. Chem. Eng. Data, 18 (1973) 54.
18 V.T. Zharov, N.D. Malegina and A.G. Morachevskii, Zh. Prikl. Khim., 38 (1965) 2132.
19 I. Nagata, J. Chem. Eng. Data, 30 (1985) 80.
20 A.G. Morachevskii and V.T. Zharov, Zh. Prikl. Khim., 36 (1963) 2771.
21 I. Nagata and H. Hayashida, J. Chem. Eng. Jpn., 3 (1970) 161.
22 R.V. Mrazek and H.C. Van Ness, AIChE J., 7 (1961) 190.
23 I. Nagata, Y. Kawamura, H. Asano, K. Fujiwara and Y. Ogasawara, Z. Phys. Chem. (Leipzig), 259 (1978) 1109.
24 I. Nagata and K. Kazuma, J. Chem. Eng. Data, 22 (1977) 79.
25 J.P.E. Grolier and A. Viallard, Int. Data Ser. A, (1973) 113.
26 I. Nagata and Y. Ogasawara, Thermochim. Acta, 52 (1982) 155.
27 I. Nagata, H. Asano and K. Fujiwara, Fluid Phase Equilibria, 1 (1977/1978) 211.
28 I. Nagata, K. Fujiwara and Y. Ogasawara, J. Chem. Thermodyn., 10 (1978) 1201.
29 J.P.E. Grolier and A. Viallard, Int. Data Ser. A, (1973) 20.
30 I. Nagata and K. Tamura, J. Chem. Thermodyn., 16 (1984) 955.
31 K.Y. Hsu and H.L. Clever, J. Chem. Thermodyn., 7 (1975) 435.
32 I. Nagata and K. Tamura, J. Chem. Thermodyn., 17 (1985) in press.
33 I. Nagata, Y. Kawamura, Y. Ogasawara and S. Tokuriki, J. Chem. Thermodyn., 12 (1980) 223.