Thermochimica Acta, 99 (1986) 145–152
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

PREDICTION OF EXCESS MOLAR ENTHALPIES FOR TERNARY ALCOHOL–SATURATED HYDROCARBON MIXTURES

ISAMU NAGATA * and KOHKI GOTOH

Department of Chemical Engineering, Kanazawa University, Kanazawa 920 (Japan)

(Received 23 August 1985)

ABSTRACT

Binary excess molar enthalpies for alcohol–alcohol mixtures are well represented by use of the UNIQUAC associated-solution model, which includes two association constants for the dimerization and polymerization of pure alcohol molecules and one solvation constant between unlike alcohol molecules and takes account of non-polar interactions. The model is further extended to predict ternary excess enthalpies for mixtures containing two alcohols and one saturated hydrocarbon with only binary parameters. Calculated results agree with the published data of many mixtures.

INTRODUCTION

Nagata [1] presented an empirical method, based on an association model, to predict the ternary excess enthalpies of mixtures including two alcohols and one saturated hydrocarbon using only binary parameters. Pando et al. [2] proposed another empirical method to correlate the excess enthalpies of binary alcohol–alcohol mixtures. Their method could not be applied to ternary alcohol–hydrocarbon mixtures. The UNIQUAC associated-solution model [3,4] has been successfully used to correlate the excess enthalpies of binary and ternary mixtures involving one alcohol. In this work the UNIQUAC associated-solution model is extended for the calculation of excess enthalpies of binary alcohol–alcohol and ternary alcohol–hydrocarbon mixtures.

ASSOCIATION MODEL FOR TERNARY ALCOHOL–SATURATED HYDROCARBON MIXTURES

A and B stand for two alcohols and C for the saturated hydrocarbon. According to a previous approach [4], the alcohols self-associate in two

---

* Author to whom correspondence should be addressed.

ways: dimerization and polymerization, and solvate each other.

$$A_1 + A_1 = A_2 \qquad K_{2A} = \frac{\phi_{A_2}}{2\phi_{A_1}^2} \tag{1}$$

$$A_i + A_1 = A_{i+1} \qquad K_A = \frac{\phi_{A_{i+1}}}{\phi_{A_i}\phi_{A_1}} \frac{i}{i+1} (i > 1) \tag{2}$$

$$B_1 + B_1 = B_2 \qquad K_{2B} = \frac{\phi_{B_2}}{2\phi_{B_1}^2} \tag{3}$$

$$B_i + B_1 = B_{i+1} \qquad K_B = \frac{\phi_{B_{i+1}}}{\phi_{B_i}\phi_{B_1}} \frac{i}{i+1} (i > 1) \tag{4}$$

$$A_i + B_j = A_iB_j \qquad K_{AB} = \frac{\phi_{A_iB_j}}{\phi_{A_i}\phi_{B_j}} \frac{ij}{r_{A_iB_j}} (i \geqslant 1,\ j \geqslant 1) \tag{5}$$

The model assumes that excess molar enthalpy of the ternary mixture is given as the sum of both chemical and physical contributions.

$$H^E = H^E_{\text{chem}} + H^E_{\text{phys}} \tag{6}$$

The chemical contribution term is defined by

$$H^E_{\text{chem}} = H_f - x_A H^*_{fA} - x_B H^*_{fB} \tag{7}$$

where H_f is the total enthalpy of complex formation in the mixture, H^*_{fA} and H^*_{fB} are the values of H_f at pure alcohol states.

$$\begin{aligned} H_f = \Bigg[& h_A \left\{ n_{A_2} + \sum_{j=1}^{\infty} n_{A_2B_j} + \sum_{i=3}^{\infty} (i-1)\left(n_{A_i} + \sum_{j=1}^{\infty} n_{A_iB_j} \right) \right\} \\ & + h_B \left\{ n_{B_2} + \sum_{i=1}^{\infty} n_{A_iB_2} + \sum_{j=3}^{\infty} (j-1)\left(n_{B_j} + \sum_{i=1}^{\infty} n_{A_iB_j} \right) \right\} \\ & + h_{AB} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} n_{A_iB_j} \Bigg] \Big/ (n_A + n_B + n_C) \end{aligned} \tag{8}$$

$$H^*_{fA} = h_A \left\{ n^*_{A_2} + \sum_{i=3}^{\infty} (i-1) n^*_{A_i} \right\} \Big/ n^*_A \tag{9}$$

$$H^*_{fB} = h_B \left\{ n^*_{B_2} + \sum_{j=3}^{\infty} (j-1) n^*_{B_j} \right\} \Big/ n^*_B \tag{10}$$

Finally H^E_{chem} is expressed in terms of the equilibrium constants, the enthalpies of hydrogen bond formation, and the monomer segment fractions.

$$H^{\mathrm{E}}_{\mathrm{chem}} = \frac{h_{\mathrm{A}} x_{\mathrm{A}} K_{2\mathrm{A}} \phi^2_{\mathrm{A}_1}}{\phi_{\mathrm{A}}(1 - K_{\mathrm{A}}\phi_{\mathrm{A}_1})^2}\left[1 + K_{\mathrm{AB}} r_{\mathrm{A}} \phi_{\mathrm{B}_1}\left\{1 + \frac{K_{2\mathrm{B}}\phi_{\mathrm{B}_1}}{(1 - K_{\mathrm{B}}\phi_{\mathrm{B}_1})}\right\}\right] + \frac{h_{\mathrm{B}} x_{\mathrm{B}} K_{2\mathrm{B}} \phi^2_{\mathrm{B}_1}}{\phi_{\mathrm{B}}(1 - K_{\mathrm{B}}\phi_{\mathrm{B}_1})^2}\left[1 + K_{\mathrm{AB}} r_{\mathrm{B}} \phi_{\mathrm{A}_1}\left\{1 + \frac{K_{2\mathrm{A}}\phi_{\mathrm{A}_1}}{(1 - K_{\mathrm{A}}\phi_{\mathrm{A}_1})}\right\}\right] - \frac{h_{\mathrm{A}} x_{\mathrm{A}} K_{2\mathrm{A}} \phi^{*2}_{\mathrm{A}_1}}{(1 - K_{\mathrm{A}}\phi^*_{\mathrm{A}_1})^2} - \frac{h_{\mathrm{B}} x_{\mathrm{B}} K_{2\mathrm{B}} \phi^{*2}_{\mathrm{B}_1}}{(1 - K_{\mathrm{B}}\phi^*_{\mathrm{B}_1})^2} \tag{11}$$

The monomer segment fractions are related to the nominal segment fractions.

$$\phi_I = \frac{x_I r_I}{\sum_J x_J r_J} \tag{12}$$

$$\phi_{\mathrm{A}} = \left[\phi_{\mathrm{A}_1} + \frac{K_{2\mathrm{A}}\phi^2_{\mathrm{A}_1}(2 - K_{\mathrm{A}}\phi_{\mathrm{A}_1})}{(1 - K_{\mathrm{A}}\phi_{\mathrm{A}_1})^2}\right]\left[1 + K_{\mathrm{AB}} r_{\mathrm{A}} \phi_{\mathrm{B}_1}\left\{1 + \frac{K_{2\mathrm{B}}\phi_{\mathrm{B}_1}}{(1 - K_{\mathrm{B}}\phi_{\mathrm{B}_1})}\right\}\right] \tag{13}$$

$$\phi_{\mathrm{B}} = \left[\phi_{\mathrm{B}_1} + \frac{K_{2\mathrm{B}}\phi^2_{\mathrm{B}_1}(2 - K_{\mathrm{B}}\phi_{\mathrm{B}_1})}{(1 - K_{\mathrm{B}}\phi_{\mathrm{B}_1})^2}\right]\left[1 + K_{\mathrm{AB}} r_{\mathrm{B}} \phi_{\mathrm{A}_1}\left\{1 + \frac{K_{2\mathrm{A}}\phi_{\mathrm{A}_1}}{(1 - K_{\mathrm{A}}\phi_{\mathrm{A}_1})}\right\}\right] \tag{14}$$

At pure alcohol states eqns. (13) and (14) reduce to

$$1 = \phi^*_{\mathrm{A}_1} + \frac{K_{2\mathrm{A}}\phi^{*2}_{\mathrm{A}_1}(2 - K_{\mathrm{A}}\phi^*_{\mathrm{A}_1})}{(1 - K_{\mathrm{A}}\phi^*_{\mathrm{A}_1})^2} \tag{15}$$

$$1 = \phi^*_{\mathrm{B}_1} + \frac{K_{2\mathrm{B}}\phi^{*2}_{\mathrm{B}_1}(2 - K_{\mathrm{B}}\phi^*_{\mathrm{B}_1})}{(1 - K_{\mathrm{B}}\phi^*_{\mathrm{B}_1})^2} \tag{16}$$

ϕ_{A_1} and ϕ_{B_1} are calculated from eqns. (13) and (14), $\phi^*_{\mathrm{A}_1}$ from eqn. (15), and $\phi^*_{\mathrm{B}_1}$ from eqn. (16).

$H^{\mathrm{E}}_{\mathrm{phys}}$ is derived from the residual term of the UNIQUAC equation [5].

$$H^{\mathrm{E}}_{\mathrm{phys}} = -R\sum_I q_I x_I \frac{\sum_J \theta_J \dfrac{\partial \tau_{JI}}{\partial(1/T)}}{\sum_J \theta_J \tau_{JI}} \tag{17}$$

where θ_I is the surface fraction of component I and τ_{JI} is related to the energy parameter a_{JI}.

$$\theta_I = \frac{q_I x_I}{\sum_J q_J x_J} \tag{18}$$

TABLE 1

Association and structural parameters for alcohols

Substance	K_{2A}	K_A	r	q
	at 50°C			
Ethanol	41.6	113.6	1.69	1.55
1-Propanol	24.0	95.0	2.23	1.98
1-Pentanol	26.7	51.5	3.31	2.85
1-Octanol	25.2	48.4	4.94	4.15
1-Decanol	20.8	42.1	6.01	5.01

$$\tau_{JI} = \exp[-a_{JI}/T] \tag{19}$$

a_{JI} is assumed to be temperature-dependent linearly.

$$a_{JI} = C_I + D_I(T - 273.15) \tag{20}$$

CALCULATED RESULTS

Binary alcohol–alcohol mixtures

The values of the association constants of dimerization and polymerization for pure alcohols were taken from a previous paper [4]. For the enthalpies of hydrogen bond formation of pure alcohols we use a single value of -23.2 kJ mol^{-1}, which is the same as the enthalpy of dilution of ethanol in n-hexane at 25°C [6]. This value is assumed to be temperature-independent and fixes the temperature dependence of the association constants according to the van't Hoff relation. Table 1 lists the association constants and pure-component molecular structural constants estimated by the method of Vera et al. [7]. Table 2 gives the values of r and q of saturated hydrocarbons. K_{AB} and h_{AB} were considered to be adjustable parameters. Table 3 shows the values of K_{AB} and h_{AB} used in data reduction. These values were obtained after many trials. Table 4 presents the binary calculated results for alcohol–alcohol and alcohol–saturated hydrocarbon mixtures.

TABLE 2

Structural parameters for hydrocarbons

Substance	r	q
Cyclohexane	3.18	2.55
n-Heptane	4.15	3.52
n-Octane	4.69	3.95
n-Tetradecane	8.19	6.75

TABLE 3

Values of K_{AB} and h_{AB}

Mixture (A–B)	K_{AB} at 50°C	$-h_{AB}$ (kJ mol^{-1})
Ethanol–1-propanol	50	36.7
Ethanol–1-pentanol	30	36.7
Ethanol–1-octanol	25	36.7
Ethanol–1-decanol	20	36.7
1-Propanol–1-pentanol	30	36.7
1-Propanol–1-octanol	20	36.7
1-Propanol–1-decanol	15	36.7

Ternary alcohol–saturated hydrocarbon mixtures

Excess molar enthalpies for 18 ternary mixtures were calculated by use of the model with the coefficients given in Table 4. Table 5 shows the absolute arithmetic mean deviations between the calculated and experimental values.

TABLE 4

Calculated results for binary mixtures 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	
Ethanol–1-propanol	15	4.2	−129.27	−571.54	−0.3887	−2.0495	8
Ethanol–1-pentanol	13	4.9	−23.62	−636.49	−0.0338	−2.2897	9
Ethanol–1-octanol	20	3.2	−349.05	−639.61	−1.3064	−2.2956	8
Ethanol–1-decanol	19	4.5	−243.04	−666.90	−0.9590	−2.3998	8
1-Propanol–1-pentanol	25	3.7	−207.75	−481.50	−0.6624	−1.7159	10
1-Propanol–1-octanol	20	4.2	−259.59	−718.95	−0.9284	−2.5997	8
1-Propanol–1-decanol	19	6.1	−207.45	−754.09	−0.7007	−2.7356	8
Ethanol–cyclohexane	20	0.8	−97.60	258.40	−0.5665	0.9085	11
Ethanol–*n*-heptane	12	6.0	105.84	243.21	0.3721	0.6525	12
Ethanol–*n*-octane	12	2.0	873.35	270.20	3.2825	0.7022	12
1-Propanol–cyclohexane	18	4.3	207.43	−150.66	0.2818	−0.4864	11
1-Propanol–*n*-heptane	13	7.2	227.11	−193.19	0.3449	−0.6003	12
1-Propanol–*n*-octane	13	7.3	202.25	−444.37	0.4957	−1.6280	12
1-Propanol–*n*-tetradecane	14	5.7	−280.41	−28.67	−1.0697	−0.2024	12
1-Pentanol–*n*-heptane	25	13.0	246.41	−471.49	0.6976	−1.6934	13
1-Pentanol–*n*-octane	13	10.7	182.60	−496.20	0.4780	−1.7802	12
1-Pentanol–*n*-tetradecane	13	4.0	128.16	−508.69	0.2526	−1.8134	12
1-Octanol–*n*-heptane	20	5.1	26.40	−358.79	0.0133	−1.3004	14
1-Octanol–*n*-octane	14	10.0	54.10	−397.61	0.1198	−1.4493	12
1-Octanol–*n*-tetradecane	14	13.8	−80.22	−319.98	−0.3615	−1.1631	12
1-Decanol–*n*-heptane	19	6.6	120.57	−290.83	3.0754	−1.0281	15
1-Decanol–*n*-octane	20	15.0	265.57	−342.78	0.7367	−1.2015	15
1-Decanol–*n*-tetradecane	14	18.3	152.21	−494.98	0.4545	−1.7942	12

TABLE 5

Predicted results for ternary alcohol–alcohol–saturated hydrocarbon mixtures at 25°C

Mixture	No. of data points	Abs. arith. mean dev.		Ref.
		ΔH^E (J mol^{-1})	$\Delta H^E/H^E$ (%)	
Ethanol–1-propanol–cyclohexane	30	19.34	7.22	11
Ethanol–1-propanol–*n*-heptane	32	26.72	6.23	16
Ethanol–1-pentanol–*n*-heptane	35	19.70	6.61	16
Ethanol–1-octanol–*n*-heptane	30	15.32	4.27	16
Ethanol–1-decanol–*n*-heptane	30	8.98	2.48	16
Ethanol–1-propanol–*n*-octane	30	17.27	4.40	16
Ethanol–1-pentanol–*n*-octane	30	41.23	12.82	16
Ethanol–1-octanol–*n*-octane	30	21.13	5.44	16
Ethanol–1-decanol–*n*-octane	30	22.94	5.94	16
1-Propanol–1-pentanol–*n*-heptane	30	9.73	2.56	16
1-Propanol–1-octanol–*n*-heptane	35	11.38	3.35	16
1-Propanol–1-decanol–*n*-heptane	30	14.95	3.81	16
1-Propanol–1-pentanol–*n*-octane	37	16.35	3.59	16
1-Propanol–1-octanol–*n*-octane	30	8.96	2.50	16
1-Propanol–1-decanol–*n*-octane	30	16.13	4.28	16
1-Propanol–1-pentanol–*n*-tetradecane	30	19.96	4.32	16
1-Propanol–1-octanol–*n*-tetradecane	35	21.58	3.94	16
1-Propanol–1-decanol–*n*-tetradecane	30	23.36	4.21	16

The largest deviation of 41.23 J mol^{-1} is obtained for ethanol–1-pentanol–*n*-octane. For the other mixtures studied here the agreement between calculated values and experimental results is acceptable. In conclusion, the proposed model is able to correlate well the excess molar enthalpies of binary alcohol–alcohol mixtures and to predict the ternary excess molar enthalpies of mixtures including two alcohols and one saturated hydrocarbon with sufficient accuracy.

ACKNOWLEDGMENTS

This work started while I. Nagata was a quest of Professors I. Kikic and P. Alessi, Istituto di Chimica Applicata e Industriale, Universita degli Studi di Trieste, Italy, in 1984. I. Nagata thanks the Consiglio Nationale delle Ricerche (Italy) and the Japan Society for the Promotion of Science for supporting his stay at the University of Trieste.

LIST OF SYMBOLS

A, B, C	alcohols and saturated hydrocarbon
A_1, A_2, A_i	monomer, dimer, and *i*-mer of alcohol A

A_iB_j	complex between alcohol A i-mer and alcohol B j-mer
a_{JI}	energy parameter
B_1, B_2, B_i	monomer, dimer, and i-mer of alcohol B
C_I, D_I	coefficients of eqn. (20)
H_f	total enthalpy of complex formation
H^E	excess molar enthalpy
h_A	enthalpy of hydrogen bond formation for alcohol A dimer and i-mer ($i > 2$)
h_{AB}	enthalpy of complex formation between unlike alcohols
h_B	enthalpy of hydrogen bond formation for alcohol B dimer and i-mer ($i > 2$)
K_{2A}, K_A	association constants of dimerization and polymerization ($i > 2$) for alcohol A
K_{AB}	solvation constant between unlike alcohol complexes
K_{2B}, K_B	association constant of dimerization and polymerization ($i > 2$) for alcohol B
n	number of moles of a particular species
q	pure-component molecular surface parameter
R	gas constant
r	pure-component molecular size parameter
T	absolute temperature
x	liquid-phase mole fraction

Greek letters

θ	surface fraction
τ_{JI}	$\exp[-a_{JI}/T]$
ϕ	segment fraction

Subscripts

A, B, C	alcohols and saturated hydrocarbon
AB	complex formation between alcohols A and B
chem	chemical
I, J	components
phys	physical

Superscript

*	pure liquid alcohol

REFERENCES

1 I. Nagata, J. Chem. Eng. Data, 20 (1975) 110.
2 C. Pando, J.A.R. Renuncio, R.W. Hanks and J.J. Christensen, Ind. Eng. Chem., Process Des. Dev., 23 (1984) 67.
3 I. Nagata and Y. Ogasawara, Thermochim. Acta, 52 (1982) 155.
4 I. Nagata and K. Inaguma, Thermochim. Acta, 97 (1986) 51.
5 D.S. Abrams and J.M. Prausnitz, Am. Inst. Chem. Eng. J., 21 (1975) 116.
6 R.H. Stokes and C. Burfitt, J. Chem. Thermodyn., 5 (1973) 236.
7 J.H. Vera, S.G. Sayegh and G.A. Ratcliffs, Fluid Phase Equilibria, 1 (1977) 113.
8 H.D. Pflug, A.E. Pope and G.C. Benson, J. Chem. Eng. Data, 13 (1968) 408.
9 M.I. Paz-Andrade, L. Romani and F. Gonzales, An. Quim., 70 (1974) 314.
10 H.H. Sun, J.J. Christensen, R.M. Izatt and R.W. Hanks, J. Chem. Thermodyn., 12 (1980) 95.
11 I. Nagata and K. Kazuma, J. Chem. Eng. Data, 22 (1977) 79.
12 R.S. Ramalho and M. Ruel, Can. J. Chem. Eng., 46 (1968) 456.
13 Salah E.M. Haman, M.K. Kumaran and G.C. Benson, J. Chem. Thermodyn., 16 (1984) 1013.
14 G. Geiseler, K. Quitzsch, J.H. Hesselbach and K. Schmidt, Z. Phys. Chem., Neue Folge, 60 (1968) 41.
15 M.K. Kumaran and G.C. Benson, J. Chem. Thermodyn., 16 (1984) 175.
16 R.S. Ramalho and M. Ruel, Can. J. Chem. Eng., 46 (1968) 467.