Thermochimica Acta, 102 (1986) 207–222
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMODYNAMICS OF ALCOHOL SOLUTIONS. EXCESS MOLAR ENTHALPIES OF BINARY AND TERNARY MIXTURES CONTAINING TWO ALCOHOLS

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(Received 3 December 1985)

ABSTRACT

The UNIQUAC associated-solution theory is used to calculate excess molar enthalpies for binary and ternary mixtures including two aliphatic alcohols. The theory postulates that linear mixed polymers are formed by consecutive solvation reactions. This approach makes it possible to reproduce excess molar enthalpies for binary alcohol–alcohol mixtures well and to predict ternary excess molar enthalpies for mixtures containing two alcohols and one saturated hydrocarbon from binary parameters alone.

INTRODUCTION

In a previous paper [1], the UNIQUAC associated-solution theory has been improved to reproduce the vapor–liquid equilibria of binary alcohol–alcohol mixtures well and to predict vapor–liquid and liquid–liquid equilibria for ternary mixtures of two alcohols with one unassociated component from binary phase equilibrium data alone. The model postulates the formation of linear multisolvated complexes from *i*-mers of two alcohols. This paper shows the quantitative quality of the new model in the correlation of binary excess molar enthalpies for alcohol–alcohol mixtures and the prediction of the ternary excess molar enthalpies of mixtures containing two alcohols and one saturated hydrocarbon from binary parameters alone.

THEORY

A, B and C stand for alcohols and a saturated hydrocarbon. We assume that alcohols self-associate and solvate each other to form linear polymers and that the equilibrium constants are independent of the degree of associa-

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0040-6031/86/$03.50

tion and solvation. The association constant K_A for the stepwise reaction $A_i + A_1 = A_{i+1}$ and K_B for $B_i + B_1 = B_{i+1}$ are defined by

$$K_A = \frac{\Phi_{A_{i+1}}}{\Phi_{A_i}\Phi_{A_1}} \frac{i}{i+1} \tag{1}$$

$$K_B = \frac{\Phi_{B_{i+1}}}{\Phi_{B_i}\Phi_{B_1}} \frac{i}{i+1} \tag{2}$$

We postulate that the solvation equilibria have the following form

$$\begin{array}{ll} A_i + B_j = A_iB_j & B_i + A_j = B_iA_j \\ A_iB_j + A_k = A_iB_jA_k & B_iA_j + B_k = B_iA_jB_k \\ A_iB_jA_k + B_l = A_iB_jA_kB_l & B_iA_jB_k + A_l = B_iA_jB_kA_l \end{array}$$

The solvation equilibrium constant for these reactions is given by K_{AB}. For the $A_iB_jA_kB_l$ forming reaction

$$K_{AB} = \frac{\Phi_{A_iB_jA_kB_l}}{\Phi_{A_iB_jA_k}\Phi_{B_l}} \frac{r_{A_iB_jA_k} r_{B_l}}{r_{A_iB_jA_kB_l} r_A r_B} \tag{3}$$

A further assumption is that the structural parameters of complex $A_iB_jA_kB_l$ are given by those of the corresponding units: $r_{A_iB_jA_kB_l} = ir_A + jr_B + kr_A + lr_B$, $q_{A_iB_jA_kB_l} = iq_A + jq_B + kq_A + lq_B$ and these relations hold for other complexes.

The UNIQUAC associated-solution theory gives the excess molar enthalpy of ternary mixtures containing two alcohols and one saturated hydrocarbon as the sum of a chemical and a physical part.

$$H^E = H^E_{\text{chem}} + H^E_{\text{phys}} \tag{4}$$

H^E_{chem} is defined as

$$H^E_{\text{chem}} = H_f - x_A H^0_{fA} - x_B H^0_{fB} \tag{5}$$

where H_f is the total enthalpy of complex formation, H^0_{fA} is the value of H_f at pure state of alcohol A and H^0_{fB} is that at pure state of alcohol B. Expressions for H_f, H^0_{fA} and H^0_{fB} are derived in the Appendix and substituting these expressions into eqn. (5) yields

$$\begin{aligned} H^E_{\text{chem}} = {} & h_A x_A \left(\frac{\overline{U}_A \Phi_{A_1}}{\Phi_A} - \overline{U}^0_A \Phi^0_{A_1} \right) + h_B x_B \left(\frac{\overline{U}_B \Phi_{B_1}}{\Phi_B} - \overline{U}^0_B \Phi^0_{B_1} \right) \\ & + \biggl[h_A \biggl\{ \frac{\overline{U}_A}{K_{AB} U_A} \left(\frac{x_B}{\Phi_B r_A} + \frac{x_A}{\Phi_A r_B} \right) + \frac{\overline{U}_A x_A \Phi_{A_1}}{\Phi_A} \left(2 - r_A r_B K^2_{AB} \Phi_{A_1} \Phi_{B_1} U_A U_B \right) \\ & \qquad + \frac{\overline{U}_A U_B x_B \Phi_{B_1}}{U_A \Phi_B} \biggr\} + h_B \biggl\{ \frac{\overline{U}_B}{K_{AB} U_B} \left(\frac{x_B}{\Phi_B r_A} + \frac{x_A}{\Phi_A r_B} \right) \\ & \qquad + \frac{\overline{U}_B x_B \Phi_{B_1}}{\Phi_B} \left(2 - r_A r_B K^2_{AB} \Phi_{A_1} \Phi_{B_1} U_A U_B \right) + \frac{U_A \overline{U}_B x_A \Phi_{A_1}}{U_B \Phi_A} \biggr\} \end{aligned}$$

$$+h_{AB}\left(\left\{\frac{x_B}{\Phi_B r_A}+\frac{x_A}{\Phi_A r_B}\right)\frac{\left(1+r_A r_B K_{AB}^2\Phi_{A_1}\Phi_{B_1}U_A U_B\right)}{K_{AB}}\right.$$

$$\left.+2\left(\frac{U_A x_A \Phi_{A_1}}{\Phi_A}+\frac{U_B x_B \Phi_{B_1}}{\Phi_B}\right)\right\}\Bigg]$$

$$\times\frac{r_A r_B K_{AB}^2\Phi_{A_1}\Phi_{B_1}U_A U_B}{\left(1-r_A r_B K_{AB}^2\Phi_{A_1}\Phi_{B_1}U_A U_B\right)^2} \tag{6}$$

where $\bar{U}_A$, U_A, $\bar{U}_B$ and U_B are expressed by

$$\bar{U}_A = K_A\Phi_{A_1}/\left(1-K_A\Phi_{A_1}\right)^2 \tag{7}$$

$$\bar{U}_A = 1/\left(1-K_A\Phi_{A_1}\right) \tag{8}$$

$$\bar{U}_B = K_B\Phi_{B_1}/\left(1-K_B\Phi_{B_1}\right)^2 \tag{9}$$

$$U_B = 1/\left(1-K_B\Phi_{B_1}\right) \tag{10}$$

The monomer segment fractions of alcohols, Φ_{A_1} and Φ_{B_1}, are obtained by simultaneous solution of the following mass balance eqns. (1)

$$\Phi_A = \bar{S}_A + \frac{r_A K_{AB}\bar{S}_A S_B}{\left(1-r_A r_B K_{AB}^2 S_A S_B\right)^2}$$

$$\times\left[2+r_B K_{AB}S_A\left(2-r_A r_B K_{AB}^2 S_A S_B\right)+r_A K_{AB}S_B\right] \tag{11}$$

$$\Phi_B = \bar{S}_B + \frac{r_B K_{AB} S_A \bar{S}_B}{\left(1-r_A r_B K_{AB}^2 S_A S_B\right)^2}$$

$$\times\left[2+r_A K_{AB}S_B\left(2-r_A r_B K_{AB}^2 S_A S_B\right)+r_B K_{AB}S_A\right] \tag{12}$$

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

$$\bar{S}_A = \Phi_{A_1}/\left(1-K_A\Phi_{A_1}\right)^2 \tag{13}$$

$$S_A = \Phi_{A_1}/\left(1-K_A\Phi_{A_1}\right) \tag{14}$$

$$\bar{S}_B = \Phi_{B_1}/\left(1-K_B\Phi_{B_1}\right)^2 \tag{15}$$

$$S_B = \Phi_{B_1}/\left(1-K_B\Phi_{B_1}\right) \tag{16}$$

Since the saturated hydrocarbon does not form any complexes with the alcohol, $\Phi_C = \Phi_{C_1}$. The monomer segment fraction of pure alcohol A, $\Phi_{A_1}^0$, is given by

$$\Phi_{A_1}^0 = \left[1+2K_A-\left(1+4K_A\right)^{1/2}\right]/2K_A^2 \tag{17}$$

$\Phi_{B_1}^0$ is obtained analogously.

The physical contribution term is derived by applying the Gibbs–Helmholtz relation to the residual term of the UNIQUAC equation [2]

$$H^{E}_{\text{phys}} = -R\sum_{I} q_I x_I \frac{\sum_{J} \theta_J \dfrac{\partial \tau_{JI}}{\partial (1/\mathrm{T})}}{\sum_{J} \theta_J \tau_{JI}} \tag{18}$$

where the surface fraction θ_{I} and the coefficient τ_{JI} are given by

$$\Phi_I = q_I x_I / \sum_J q_J x_J \tag{19}$$

$$\tau_{JI} = \exp(-a_{JI}/T) \tag{20}$$

and a_{JI} could be expressed by a linear function of temperature.

$$a_{JI} = C_I + D_I(T - 273.15) \tag{21}$$

CALCULATED RESULTS

Binary mixtures

The association constants at 50°C for pure normal aliphatic alcohols were obtained from Brandani [3]: 110.4 for ethanol; 87.0 for 1-propanol; 47.7 for 1-pentanol; 39.5 for 1-octanol; 36.8 for 1-decanol. The enthalpy of hydrogen bond formation in pure alcohols is taken as -23.2 kJ mol^{-1}, which is equivalent to the enthalpy of dilution of ethanol in *n*-hexane at 25°C [4]. This value is assumed to be temperature-independent and provides the temperature dependence of the association constant by means of the van't Hoff equation. The pure-component structural parameters were calculated by using the method of Vera et al. [5]. Table 1 lists the solvation constants and enthalpies of complex formation. Table 2 shows the calculated results

TABLE 1

Solvation constants and enthalpies of complex formation

Mixture (A–B)	K_{AB} at 50°C	$-h_{AB}$ (kJ mol^{-1})
Ethanol–1-propanol	49	23.2
Ethanol–1-pentanol	27	23.2
Ethanol–1-octanol	16	23.2
Ethanol–1-decanol	13	23.2
1-Propanol–1-pentanol	22	23.2
1-Propanol–1-octanol	14	23.2
1-Propanol–1-decanol	10	23.2

TABLE 2

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				Reference
			C_A (K)	C_B (K)	D_A	D_B	
Ethanol–1-propanol	15	2.1	0	0	0	0	7
Ethanol–1-pentanol	13	4.2	0	0	0	0	8
Ethanol–1-octanol	20	1.4	270.30	−92.35	2.7320	−0.5498	7
Ethanol–1-decanol	19	4.0	113.66	−341.02	0.0428	−1.0865	7
1-Propanol–1-pentanol	25	3.3	0	0	0	0	9
1-Propanol–1-octanol	20	0.7	101.48	−19.91	0.1834	−0.6204	7
1-Propanol–1-decanol	19	1.7	183.52	−335.68	0.4200	−1.1179	7
Ethanol–cyclohexane	20	2.1	15.19	−160.95	−0.5433	−0.2478	10
Ethanol–*n*-heptane	12	7.9	94.02	−17.42	1.3992	−0.8914	11
Ethanol–*n*-octane	12	4.1	300.97	130.52	1.4496	0.1941	11
1-Propanol–cyclohexane	18	4.9	182.97	−219.29	0.1587	−0.6248	10
1-Propanol–*n*-heptane	13	7.1	50.51	−20.98	0.4914	−0.3822	11
1-Propanol–*n*-octane	13	7.7	270.22	−113.17	1.1881	−0.5423	11
1-Propanol–*n*-tetradecane	14	7.0	84.07	−40.46	1.7224	−1.1943	11
1-Pentanol–*n*-heptane	14	13.2	215.35	−110.50	1.0058	−0.5260	11
1-Pentanol–*n*-octane	13	14.2	363.60	−100.01	1.5311	−0.4515	11
1-Pentanol–*n*-tetradecane	13	6.2	221.89	−212.91	2.8504	−1.5965	11
1-Octanol–*n*-heptane	20	5.8	315.20	−36.30	1.2949	−0.2105	12
1-Octanol–*n*-octane	14	11.9	19.86	−176.02	−0.0413	−0.5731	11
1-Octanol–*n*-tetradecane	14	16.5	192.18	−13.48	0.0896	−0.1925	11
1-Decanol–*n*-heptane	19	6.9	283.76	−61.73	1.1587	−0.2953	13
1-Decanol–*n*-octane	20	9.2	118.10	−305.49	0.3267	−1.0721	13
1-Decanol–*n*-tetradecane	14	18.3	105.39	14.87	0.5739	−0.1065	11

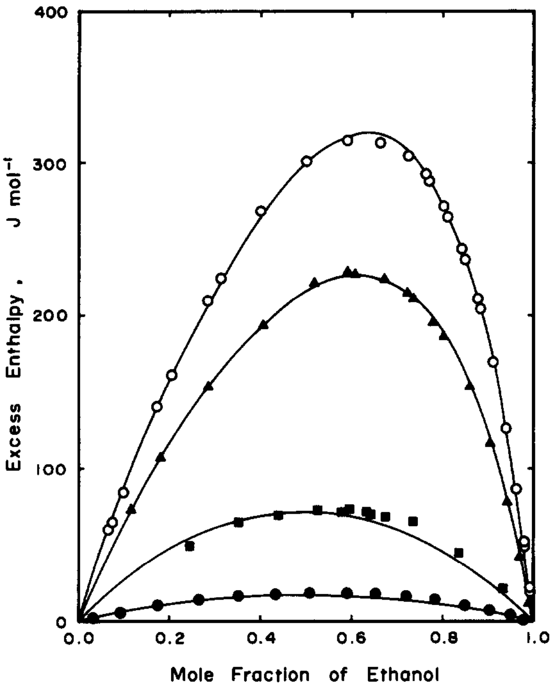

Fig. 1. Comparison of experimental and calculated excess molar enthalpies for mixtures containing ethanol at 25°C. Calculated (———). Experimental: ●, ethanol–1-propanol [7]; ■, ethanol–1-pentanol [8]; ▲, ethanol–1-octanol [7]; ○, ethanol–1-decanol [7].

obtained for binary alcohol–alcohol and alcohol–saturated hydrocarbon mixtures. In ethanol–1-propanol, ethanol–1-pentanol and 1-propanol–1-pentanol mixtures, the physical contribution was neglected and only the chemical contribution was allowed for. If alcohols differ significantly from each other as to the number of carbon atoms present in their molecules, the chemical contribution is not sufficient for nonideality and the physical contribution term must be included for good description of the excess enthalpy for alcohol–alcohol mixtures. The calculated results are compared with the experimental data of alcohol–alcohol mixtures in Figs. 1 and 2.

Ternary alcohol–saturated hydrocarbon mixtures

Table 3 presents the ternary predicted results for 18 mixtures containing two alcohols and one saturated hydrocarbon by using the binary parameters listed in Tables 1 and 2, together with those previously obtained by Nagata and Gotoh [6], who assumed only the formation of A_iB_j. Table 3 shows clearly that the present model gives generally the smaller deviations between the calculated and experimental excess molar enthalpies than those of the previous model [6], except for that of 1-propanol–1-octanol–*n*-octane.

TABLE 3

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

Mixture	No. of data points	Abs. arith. mean deviations				Reference
		ΔH^E (J mol^{-1})		$\Delta H^E/H^E$ (%)		
		I [a]	II [b]	I [a]	II [b]	
Ethanol–1-propanol–cyclohexane	2	6.83	19.38	1.76	7.22	10
Ethanol–1-propanol–*n*-heptane	32	12.38	26.72	2.89	6.23	14
Ethanol–1-pentanol–*n*-heptane	35	11.96	19.70	4.23	6.61	14
Ethanol–1-octanol–*n*-heptane	30	6.18	15.32	1.50	4.27	14
Ethanol–1-decanol–*n*-heptane	30	4.72	8.98	1.13	2.48	14
Ethanol–1-propanol–*n*-octane	30	6.54	17.27	2.01	4.40	14
Ethanol–1-pentanol–*n*-octane	30	18.08	41.23	4.95	12.82	14
Ethanol–1-octanol–*n*-octane	30	18.77	21.13	5.03	5.44	14
Ethanol–1-decanol–*n*-octane	30	19.98	22.94	5.49	5.94	14
1-Propanol–1-pentanol–*n*-heptane	30	8.25	9.73	2.77	2.56	14
1-Propanol–1-octanol–*n*-heptane	35	8.46	11.38	3.03	3.35	14
1-Propanol–1-decanol–*n*-heptane	30	7.20	14.95	1.72	3.81	14
1-Propanol–1-pentanol–*n*-octane	37	14.41	16.35	3.55	3.59	14
1-Propanol–1-octanol–*n*-octane	30	11.60	8.96	3.26	2.50	14
1-Propanol–1-decanol–*n*-octane	30	8.52	16.13	2.05	4.28	14
1-Propanol–1-pentanol–*n*-tetradecane	30	10.61	19.96	2.63	4.32	14
1-Propanol–1-octanol–*n*-tetradecane	35	9.19	21.58	2.39	3.94	14
1-Propanol–1-decanol–*n*-tetradecane	30	10.42	23.36	1.67	4.21	14
Overall mean deviation		10.79	18.62	2.89	4.89	

[a] I, this work.

[b] II, Nagata and Gotoh [6].

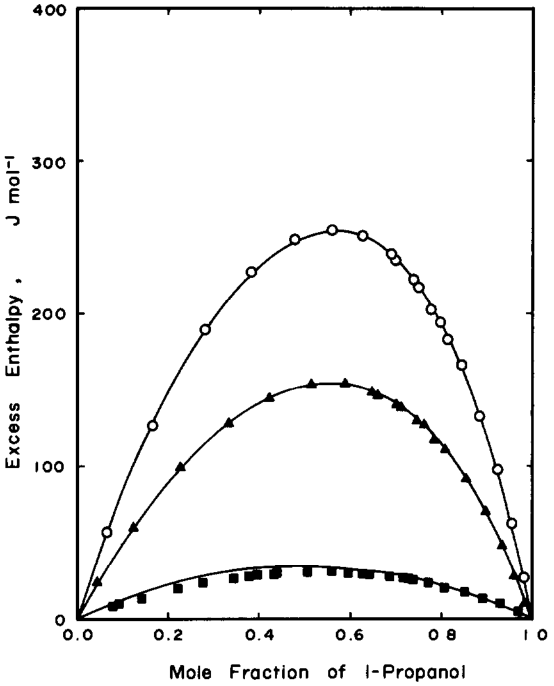

Fig. 2. Comparison of experimental and calculated excess molar enthalpies for mixtures containing 1-propanol at 25°C. Calculated (———). Experimental: ■, 1-propanol–1-pentanol [9]; ▲, 1-propanol–1-octanol [7]; ○, 1-propanol–1-decanol [7].

Pando et al. [15] proposed an association model for the excess enthalpy of binary alcohol–alcohol mixtures and did not apply the model to ternary mixtures containing two alcohols and one saturated hydrocarbon.

In conclusion, the present model has good quality in the correlation of excess molar enthalpies for binary alcohol–alcohol mixtures as well as the prediction of ternary excess molar enthalpies for mixtures containing two alcohols and one saturated hydrocarbon.

LIST OF SYMBOLS

A, B, C	alcohols and saturated hydrocarbon
A_1, A_i	monomer and *i*-mer of alcohol A
A_iB_j	complex composed of alcohol A *i*-mer and alcohol B *j*-mer
a_{JI}	binary interaction parameter
B_1, B_i	monomer and *i*-mer of alcohol B
C_I, D_I	coefficients of eqn. (21)
H_f	total enthalpy of complex formation
H^E	excess molar enthalpy
h_A, h_B	enthalpies of hydrogen bond formation of alcohols A and B

h_{AB}	enthalpy of complex formation between unlike alcohols
K_A, K_B	association constants for pure alcohols A and B
K_{AB}	solvation constant between alcohol complexes
n	number of moles of a particular species
q_I	molecular geometric area parameter of pure component I
R	gas constant
r_I	molecular geometric volume parameter of pure component I
$\underline{S}_A$, $\underline{S}_B$	sums as defined by eqns. (14) and (16)
$\bar{S}_A$, $\bar{S}_B$	sums as defined by eqns. (13) and (15)
T	absolute temperature
$\underline{U}_A$, $\underline{U}_B$	quantities as defined by eqns. (8) and (10)
$\bar{U}_A$, $\bar{U}_B$	quantities as defined by eqns. (7) and (9)
x_I	liquid-phase mole fraction of component I

Greek letters

θ_I	surface fraction of component I
τ_{JI}	coefficient as defined by $\exp(-a_{JI}/T)$
Φ_I	segment fraction of component I
Φ_{I_1}	monomer segment fraction of component I

Subscripts

A, B, C	components A, B and C
A_1, B_1, C_1	monomers of components A, B and C
AB	binary complex
A_iB_j	complex containing i molecules of alcohol A and j molecules of alcohol B
chem	chemical
I, J	components
i, j, k, l, m	i, j, k, l and m-mers of the alcohol
phys	physical

Superscript

^{0}	pure alcohol reference state

APPENDIX

We consider one mole of the ternary alcohol solution. The total enthalpy of formation of the complexes from alcohol A and alcohol B is expressed by

$$
\begin{aligned}
H_{\mathrm{f}} = h_{\mathrm{A}}\Big\{ & \sum_{i}(i-1)n_{\mathrm{A}_i} + \sum_{i}\sum_{j}(i-1)n_{\mathrm{A}_i\mathrm{B}_j} + \sum_{i}\sum_{j}\sum_{k}[(i-1)+(k-1)]\,n_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k} \\
& + \sum_{i}\sum_{j}\sum_{k}\sum_{l}[(i-1)+(k-1)]\,n_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{B}_l} + \cdots \\
& + \sum_{i}\sum_{j}(j-1)n_{\mathrm{B}_i\mathrm{A}_j} + \sum_{i}\sum_{j}\sum_{k}(j-1)n_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k} \\
& + \sum_{i}\sum_{j}\sum_{k}\sum_{l}[(j-1)+(l-1)]\,n_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{A}_l} + \cdots \Big\} \\
& + h_{\mathrm{B}}\Big\{\sum_{i}(i-1)n_{\mathrm{B}_i} + \sum_{i}\sum_{j}(i-1)n_{\mathrm{B}_i\mathrm{A}_j} + \sum_{i}\sum_{j}\sum_{k}[(i-1) \\
& + (k-1)]\,n_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k} + \sum_{i}\sum_{j}\sum_{k}\sum_{l}[(i-1)+(k-1)]\,n_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{A}_l} + \cdots \\
& + \sum_{i}\sum_{j}(j-1)n_{\mathrm{A}_i\mathrm{B}_j} + \sum_{i}\sum_{j}\sum_{k}(j-1)n_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k} \\
& + \sum_{i}\sum_{j}\sum_{k}\sum_{l}[(j-1)+(l-1)]\,n_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{B}_l} + \cdots \Big\} \\
& + h_{\mathrm{AB}}\Big\{\sum_{i}\sum_{j}n_{\mathrm{A}_i\mathrm{B}_j} + 2\sum_{i}\sum_{j}\sum_{k}n_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k} + 3\sum_{i}\sum_{j}\sum_{k}\sum_{l}n_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{B}_l} \\
& + 4\sum_{i}\sum_{j}\sum_{k}\sum_{l}\sum_{m}n_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{B}_l\mathrm{A}_m} + \cdots \\
& + \sum_{i}\sum_{j}n_{\mathrm{B}_i\mathrm{A}_j} + 2\sum_{i}\sum_{j}\sum_{k}n_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k} + 3\sum_{i}\sum_{j}\sum_{k}\sum_{l}n_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{A}_l} \\
& + 4\sum_{i}\sum_{j}\sum_{k}\sum_{l}\sum_{m}n_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{A}_l\mathrm{B}_m} + \cdots \Big\} \\
= {} & h_{\mathrm{A}}(S_1+S_2) + h_{\mathrm{B}}(S_3+S_4) + h_{\mathrm{AB}}S_5
\end{aligned}
\tag{A1}
$$

where n is the number of moles of a particular complex and we differentiate linearly solvated alcohol complexes $(\mathrm{A}_i\mathrm{B}_j)_k$ and $(\mathrm{B}_i\mathrm{A}_j)_k$, where the indices i, j and k go from one to infinity, because in the former a free hydroxyl group is attached to B, which is the tail molecule of $(\mathrm{A}_i\mathrm{B}_j)_k$ and in the latter it belongs to A, the tail one of $(\mathrm{B}_i\mathrm{A}_j)_k$.

S_1, S_2, S_3, S_4 and S_5 are derived as described below.

$$
\begin{aligned}
S_1 &= \sum_{i}(i-1)n_{\mathrm{A}_i} = n_{\mathrm{A}_1}\sum_{i}(i-1)\left(K_{\mathrm{A}}\Phi_{\mathrm{A}_1}\right)^{i-1} \\
&= K_{\mathrm{A}}\Phi_{\mathrm{A}_1}n_{\mathrm{A}_1}/\left(1-K_{\mathrm{A}}\Phi_{\mathrm{A}_1}\right)^2 = \overline{U}_{\mathrm{A}}n_{\mathrm{A}_1}
\end{aligned}
\tag{A2}
$$

$$\begin{aligned}
S_2 = {} & \sum_i \sum_j (i-1) n_{\mathrm{A}_i\mathrm{B}_j} + \sum_i \sum_j \sum_k [(i-1)+(k-1)]\, n_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k} \\
& + \sum_i \sum_j \sum_k \sum_l [(i-1)+(k-1)]\, n_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{B}_l} \\
& + \sum_i \sum_j \sum_k \sum_l \sum_m [(i-1)+(k-1)+(m-1)]\, n_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{B}_l\mathrm{A}_m} + \cdots \\
& + \sum_i \sum_j (j-1) n_{\mathrm{B}_i\mathrm{A}_j} + \sum_i \sum_j \sum_k (j-1) n_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k} \\
& + \sum_i \sum_j \sum_k \sum_l [(j-1)+(l-1)]\, n_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{A}_l} \\
& + \sum_i \sum_j \sum_k \sum_l \sum_m [(j-1)+(l-1)]\, n_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{A}_l\mathrm{B}_m} + \cdots \\
= {} & \frac{K'_{\mathrm{AB}}}{V} \sum_i (i-1) n_{\mathrm{A}_i} \sum_j n_{\mathrm{B}_j} + \frac{K'^2_{\mathrm{AB}}}{V^2} \left[\sum_i (i-1) n_{\mathrm{A}_i} \sum_j n_{\mathrm{B}_j} \sum_k n_{\mathrm{A}_k} \right. \\
& \left. + \sum_i n_{\mathrm{A}_i} \sum_j n_{\mathrm{B}_j} \sum_k (k-1) n_{\mathrm{A}_k} \right] + \frac{K'^3_{\mathrm{AB}}}{V^3} \left[\sum_i (i-1) n_{\mathrm{A}_i} \sum_j n_{\mathrm{B}_j} \sum_k n_{\mathrm{A}_k} \sum_l n_{\mathrm{B}_l} \right. \\
& \left. + \sum_i n_{\mathrm{A}_i} \sum_j n_{\mathrm{B}_j} \sum_k (k-1) n_{\mathrm{A}_k} \sum_l n_{\mathrm{B}_l} \right] \\
& + \frac{K'^4_{\mathrm{AB}}}{V^4} \left[\sum_i (i-1) n_{\mathrm{A}_i} \sum_j n_{\mathrm{B}_j} \sum_k n_{\mathrm{A}_k} \sum_l n_{\mathrm{B}_l} \sum_m n_{\mathrm{A}_m} \right. \\
& + \sum_i n_{\mathrm{A}_i} \sum_j n_{\mathrm{B}_j} \sum_k (k-1) n_{\mathrm{A}_k} \sum_l n_{\mathrm{B}_l} \sum_m n_{\mathrm{A}_m} \\
& \left. + \sum_i n_{\mathrm{A}_i} \sum_j n_{\mathrm{B}_j} \sum_k n_{\mathrm{A}_k} \sum_l n_{\mathrm{B}_l} \sum_m (m-1) n_{\mathrm{A}_m} \right] + \ldots \\
& + \frac{K'_{\mathrm{AB}}}{V} \sum_i n_{\mathrm{B}_i} \sum_j (j-1) n_{\mathrm{A}_j} + \frac{K'^2_{\mathrm{AB}}}{V^2} \sum_i n_{\mathrm{B}_i} \sum_j (j-1) n_{\mathrm{A}_j} \sum_k n_{\mathrm{B}_k} \\
& + \frac{K'^3_{\mathrm{AB}}}{V^3} \left[\sum_i n_{\mathrm{B}_i} \sum_j (j-1) n_{\mathrm{A}_j} \sum_k n_{\mathrm{B}_k} \sum_l n_{\mathrm{A}_l} + \sum_i n_{\mathrm{B}_i} \sum_j n_{\mathrm{A}_j} \sum_k n_{\mathrm{B}_k} \sum_l (l-1) n_{\mathrm{A}_l} \right] \\
& + \frac{K'^4_{\mathrm{AB}}}{V^4} \left[\sum_i n_{\mathrm{B}_i} \sum_j (j-1) n_{\mathrm{A}_j} \sum_k n_{\mathrm{B}_k} \sum_l n_{\mathrm{A}_l} \sum_m n_{\mathrm{B}_m} \right. \\
& \left. + \sum_i n_{\mathrm{B}_i} \sum_j n_{\mathrm{A}_j} \sum_k n_{\mathrm{B}_k} \sum_l (l-1) n_{\mathrm{A}_l} \sum_m n_{\mathrm{B}_m} \right] + \ldots
\end{aligned}$$

where $K'_{\mathrm{AB}} = r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}}$ and V is the true molar volume of the solution. We insert $\bar{U}_A$, U_A, $\bar{U}_B$ and U_B as defined by eqns. (7–10), $\Phi_{A_1} = r_A n_{A_1}/V$ and $\Phi_{B_1} = r_B n_{B_1}/V$ into the above equation.

$$\begin{aligned}
S_2 &= \frac{K'_{AB}}{r_A}\Phi_{A_1} n_{B_1}\bar{U}_A U_B + \frac{2K'^2_{AB}}{r_A r_B}\Phi_{A_1}\Phi_{B_1} n_{A_1}\bar{U}_A U_B U_A + \frac{2K'^3_{AB}}{r_A^2 r_B}\Phi^2_{A_1}\Phi_{B_1} n_{B_1}\bar{U}_A U_B^2 U_A \\
&\quad + \frac{3K'^4_{AB}}{r_A^2 r_B^2}\Phi^2_{A_1}\Phi^2_{B_1} n_{A_1}\bar{U}_A U_B^2 U_A^2 + \ldots + \frac{K'_{AB}}{r_B}\Phi_{B_1} n_{A_1}\bar{U}_A U_B \\
&\quad + \frac{K'^2_{AB}}{r_B r_A}\Phi_{B_1}\Phi_{A_1} n_{B_1}\bar{U}_A U_B^2 + \frac{2K'^3_{AB}}{r_B^2 r_A}\Phi^2_{B_1}\Phi_{A_1} n_{A_1}\bar{U}_A U_B^2 U_A \\
&\quad + \frac{2K'^4_{AB}}{r_B^2 r_A^2}\Phi^2_{B_1}\Phi^2_{A_1} n_{B_1}\bar{U}_A U_B^3 U_A + \ldots \\
&= r_B K_{AB}\Phi_{A_1} n_{B_1}\bar{U}_A U_B \sum_i i\left(r_A r_B K^2_{AB}\Phi_{A_1}\Phi_{B_1} U_A U_B\right)^{i-1} \\
&\quad + \bar{U}_A n_{A_1}\sum_i (i+1)\left(r_A r_B K^2_{AB}\Phi_{A_1}\Phi_{B_1} U_A U_B\right)^{i} \\
&\quad + r_A K_{AB}\Phi_{B_1} n_{A_1}\bar{U}_A U_B \sum_i i\left(r_A r_B K^2_{AB}\Phi_{A_1}\Phi_{B_1} U_A U_B\right)^{i-1} \\
&\quad + \frac{\bar{U}_A}{U_A} U_B n_{B_1}\sum_i i\left(r_A r_B K^2_{AB}\Phi_{A_1}\Phi_{B_1} U_A U_B\right)^{i} \\
&= \left[\frac{\bar{U}_A}{K_{AB}U_A}\left(\frac{n_{B_1}}{r_A\Phi_{B_1}} + \frac{n_{A_1}}{r_B\Phi_{A_1}}\right) + \bar{U}_A n_{A_1}\left(2 - r_A r_B K^2_{AB}\Phi_{A_1}\Phi_{B_1} U_A U_B\right) + \frac{\bar{U}_A U_B n_{B_1}}{U_A}\right] \\
&\quad \times \frac{r_A r_B K^2_{AB}\Phi_{A_1}\Phi_{B_1} U_A U_B}{\left(1 - r_A r_B K^2_{AB}\Phi_{A_1}\Phi_{B_1} U_A U_B\right)^2} \qquad \text{(A3)}
\end{aligned}$$

Similarly we can derive the sums of S_3, S_4 and S_5.

$$S_3 = \sum_i (i-1) n_{B_i} = K_B\Phi_{B_1} n_{B_1}/\left(1 - K_B\Phi_{B_1}\right)^2 = \bar{U}_B n_{B_1} \qquad \text{(A4)}$$

$$\begin{aligned}
S_4 &= \sum_i\sum_j (i-1) n_{B_iA_j} + \sum_i\sum_j\sum_k [(i-1) + (k-1)]\, n_{B_iA_jB_k} \\
&\quad + \sum_i\sum_j\sum_k\sum_l [(i-1) + (k-1)]\, n_{B_iA_jB_kA_l} \\
&\quad + \sum_i\sum_j\sum_k\sum_l\sum_m [(i-1) + (k-1) + (m-1)]\, n_{B_iA_jB_kA_lB_m} + \ldots \\
&\quad + \sum_i\sum_j (j-1) n_{A_iB_j} + \sum_i\sum_j\sum_k (j-1) n_{A_iB_jA_k}
\end{aligned}$$

$$
\begin{aligned}
&+\sum_i\sum_j\sum_k\sum_l[(j-1)+(l-1)]\,n_{A_iB_jA_kB_l}\\
&+\sum_i\sum_j\sum_k\sum_l\sum_m[(j-1)+(l-1)]\,n_{A_iB_jA_kB_lA_m}+\ldots\\
&=\left[\frac{\overline{U}_B}{K_{AB}U_B}\left(\frac{n_{B_1}}{r_A\Phi_{B_1}}+\frac{n_{A_1}}{r_B\Phi_{A_1}}\right)+\overline{U}_Bn_{B_1}\left(2-r_Ar_BK_{AB}^2\Phi_{A_1}\Phi_{B_1}U_AU_B\right)+\frac{\overline{U}_BU_An_{A_1}}{U_B}\right]\\
&\quad\times\frac{r_Ar_BK_{AB}^2\Phi_{A_1}\Phi_{B_1}U_AU_B}{\left(1-r_Ar_BK_{AB}^2\Phi_{A_1}\Phi_{B_1}U_AU_B\right)^2}
\end{aligned}
\tag{A5}
$$

$$
\begin{aligned}
S_5&=\sum_i\sum_j n_{A_iB_j}+2\sum_i\sum_j\sum_k n_{A_iB_jA_k}+3\sum_i\sum_j\sum_k\sum_l n_{A_iB_jA_kB_l}\\
&\quad+4\sum_i\sum_j\sum_k\sum_l\sum_m n_{A_iB_jA_kB_lA_m}+\ldots+\sum_i\sum_j n_{B_iA_j}+2\sum_i\sum_j\sum_k n_{B_iA_jB_k}\\
&\quad+3\sum_i\sum_j\sum_k\sum_l n_{B_iA_jB_kA_l}+4\sum_i\sum_j\sum_k\sum_l\sum_m n_{B_iA_jB_kA_lB_m}+\ldots\\
&=\frac{K'_{AB}}{V}\sum_i n_{A_i}\sum_j n_{B_j}+\frac{2K'^2_{AB}}{V^2}\sum_i n_{A_i}\sum_j n_{B_j}\sum_k n_{A_k}\\
&\quad+\frac{3K'^3_{AB}}{V^3}\sum_i n_{A_i}\sum_j n_{B_j}\sum_k n_{A_k}\sum_l n_{B_l}+\frac{4K'^4_{AB}}{V^4}\sum_i n_{A_i}\sum_j n_{B_j}\sum_k n_{A_k}\sum_l n_{B_l}\sum_m n_{A_m}+\ldots\\
&\quad+\frac{K'_{AB}}{V}\sum_i n_{B_i}\sum_j n_{A_j}+\frac{2K'^2_{AB}}{V^2}\sum_i n_{B_i}\sum_j n_{A_j}\sum_k n_{B_k}\\
&\quad+\frac{3K'^3_{AB}}{V^3}\sum_i n_{B_i}\sum_j n_{A_j}\sum_k n_{B_k}\sum_l n_{A_l}+\frac{4K'^4_{AB}}{V^4}\sum_i n_{B_i}\sum_j n_{A_j}\sum_k n_{B_k}\sum_l n_{A_l}\sum_m n_{B_m}+\ldots\\
&=\frac{K'_{AB}}{r_A}\Phi_{A_1}n_{B_1}U_AU_B+\frac{2K'^2_{AB}}{r_Ar_B}\Phi_{A_1}\Phi_{B_1}n_{A_1}U_A^2U_B+\frac{3K'^3_{AB}}{r_A^2r_B}\Phi_{A_1}^2\Phi_{B_1}n_{B_1}U_A^2U_B^2\\
&\quad+\frac{4K'^4_{AB}}{r_A^2r_B^2}\Phi_{A_1}^2\Phi_{B_1}^2n_{A_1}U_A^3U_B^2+\ldots+\frac{K'_{AB}}{r_B}\Phi_{B_1}n_{A_1}U_BU_A+\frac{2K'^2_{AB}}{r_Br_A}\\
&\quad\times\Phi_{B_1}\Phi_{A_1}n_{B_1}U_B^2U_A+\frac{3K'^3_{AB}}{r_B^2r_A}\Phi_{B_1}^2\Phi_{A_1}n_{A_1}U_B^2U_A^2+\frac{4K'^4_{AB}}{r_B^2r_A^2}\Phi_{B_1}^2\Phi_{A_1}^2n_{B_1}U_B^3U_A^2+\ldots\\
&=\frac{n_{B_1}}{K_{AB}r_A\Phi_{B_1}}\sum_i(2i-1)\left(r_Ar_BK_{AB}^2\Phi_{A_1}\Phi_{B_1}U_AU_B\right)^i\\
&\quad+U_An_{A_1}\sum_i 2i\left(r_Ar_BK_{AB}^2\Phi_{A_1}\Phi_{B_1}U_AU_B\right)^i+\frac{n_{A_1}}{K_{AB}r_B\Phi_{A_1}}\sum_i(2i-1)\\
&\quad\times\left(r_Ar_BK_{AB}^2\Phi_{A_1}\Phi_{B_1}U_AU_B\right)^i+U_Bn_{B_1}\sum_i 2i\left(r_Ar_BK_{AB}^2\Phi_{A_1}\Phi_{B_1}U_AU_B\right)^i
\end{aligned}
$$

$$= \left[\left(\frac{n_{\mathrm{B}_1}}{r_{\mathrm{A}}\Phi_{\mathrm{B}_1}} + \frac{n_{\mathrm{A}_1}}{r_{\mathrm{B}}\Phi_{\mathrm{A}_1}}\right)\frac{\left(1 + r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2\Phi_{\mathrm{A}_1}\Phi_{\mathrm{B}_1}U_{\mathrm{A}}U_{\mathrm{B}}\right)}{K_{\mathrm{AB}}}\right.$$

$$\left. + 2\left(U_{\mathrm{A}}n_{\mathrm{A}_1} + U_{\mathrm{B}}n_{\mathrm{B}_1}\right)\right]\frac{r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2\Phi_{\mathrm{A}_1}\Phi_{\mathrm{B}_1}U_{\mathrm{A}}U_{\mathrm{B}}}{\left(1 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2\Phi_{\mathrm{A}_1}\Phi_{\mathrm{B}_1}U_{\mathrm{A}}U_{\mathrm{B}}\right)^2} \qquad \text{(A6)}$$

It is necessary to express n_{A_i} in terms of Φ_{A_1}, x_{A} and Φ_{A}. The following molecular balances can be written.

$$x_{\mathrm{A}} = N_1 + N_2 + N_3 + \ldots = \sum_i N_i$$

$$= \sum_i i n_{\mathrm{A}_i} + \sum_i \sum_j i n_{\mathrm{A}_i\mathrm{B}_j} + \sum_i \sum_j \sum_k (i+k) n_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k}$$

$$+ \sum_i \sum_j \sum_k \sum_l (i+k) n_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{B}_l} + \ldots + \sum_i \sum_j j n_{\mathrm{B}_i\mathrm{A}_j}$$

$$+ \sum_i \sum_j \sum_k j n_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k} + \sum_i \sum_j \sum_k \sum_l (j+1) n_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{A}_l} + \ldots \qquad \text{(A7)}$$

$$\Phi_{\mathrm{A}} = F_1 + F_2 + F_3 + \ldots = \sum_i F_i$$

$$= \sum_i \Phi_{\mathrm{A}_i} + \sum_i \sum_j \Phi_{\mathrm{A}_i\mathrm{B}_j}\frac{r_{\mathrm{A}_i}}{r_{\mathrm{A}_i\mathrm{B}_j}} + \sum_i \sum_j \sum_k \Phi_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k}\frac{r_{\mathrm{A}_i\mathrm{A}_k}}{r_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k}}$$

$$+ \sum_i \sum_j \sum_k \sum_l \Phi_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{B}_l}\frac{r_{\mathrm{A}_i\mathrm{A}_k}}{r_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{B}_l}} + \ldots$$

$$+ \sum_i \sum_j \Phi_{\mathrm{B}_i\mathrm{A}_j}\frac{r_{\mathrm{A}_j}}{r_{\mathrm{B}_i\mathrm{A}_j}} + \sum_i \sum_j \sum_k \Phi_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k}\frac{r_{\mathrm{A}_i}}{r_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k}}$$

$$+ \sum_i \sum_j \sum_k \sum_l \Phi_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{A}_l}\frac{r_{\mathrm{A}_i\mathrm{A}_k}}{r_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{A}_l}} + \ldots \qquad \text{(A8)}$$

where

$$N_1 = \sum_i i n_{\mathrm{A}_i} \qquad \text{(A9)}$$

$$F_1 = \sum_i \Phi_{\mathrm{A}_i} = \sum_i n_{\mathrm{A}_i} r_{\mathrm{A}_i}/V = \sum_i i r_{\mathrm{A}} n_{\mathrm{A}_i}/V = \frac{r_{\mathrm{A}}}{V}\sum_i i n_{\mathrm{A}_i} \qquad \text{(A10)}$$

$$N_2 = \sum_i \sum_j i n_{\mathrm{A}_i\mathrm{B}_j} \qquad \text{(A11)}$$

$$F_2 = \sum_i \sum_j \Phi_{\mathrm{A}_i\mathrm{B}_j}\frac{r_{\mathrm{A}_i}}{r_{\mathrm{A}_i\mathrm{B}_j}} = \frac{r_{\mathrm{A}}}{V}\sum_i \sum_j i n_{\mathrm{A}_i\mathrm{B}_j} \qquad \text{(A12)}$$

$$N_3 = \sum_i \sum_j \sum_k (i+k) n_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k} \qquad \text{(A13)}$$

$$F_3 = \sum_i \sum_j \sum_k \Phi_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k} \frac{r_{\mathrm{A}_i\mathrm{A}_k}}{r_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k}} = \sum_i \sum_j \sum_k \frac{n_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k} r_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k}}{V} \frac{(i+k) r_\mathrm{A}}{r_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k}}$$

$$= \frac{r_\mathrm{A}}{V} \sum_i \sum_j \sum_k (i+k) n_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k} \tag{A14}$$

and so on.

Then the ratio of N_i to F_i gives

$$\frac{N_1}{F_1} = \frac{N_2}{F_2} = \frac{N_3}{F_3} = \frac{N_1 + N_2 + N_3 + \dots}{F_1 + F_2 + F_3 + \dots} = \frac{x_\mathrm{A}}{\Phi_\mathrm{A}} = \frac{V}{r_\mathrm{A}} = \frac{n_{\mathrm{A}_1}}{\Phi_{\mathrm{A}_1}} \tag{A15}$$

In the same way as described above, we can obtain

$$\frac{x_\mathrm{B}}{\Phi_\mathrm{B}} = \frac{n_{\mathrm{B}_1}}{\Phi_{\mathrm{B}_1}} \tag{A16}$$

Inserting eqns. (A2–A6), (A15) and (A16) into eqn. (A1) yields

$$\begin{aligned} H_\mathrm{f} = {} & h_\mathrm{A} x_\mathrm{A} \bar{U}_\mathrm{A} \frac{\Phi_{\mathrm{A}_1}}{\Phi_\mathrm{A}} + h_\mathrm{B} x_\mathrm{B} \bar{U}_\mathrm{B} \frac{\Phi_{\mathrm{B}_1}}{\Phi_\mathrm{B}} \\ & + \Bigg\{ h_\mathrm{A} \Bigg[\frac{\bar{U}_\mathrm{A}}{K_\mathrm{AB} U_\mathrm{A}} \left(\frac{x_\mathrm{B}}{\Phi_\mathrm{B} r_\mathrm{A}} + \frac{x_\mathrm{A}}{\Phi_\mathrm{A} r_\mathrm{B}} \right) + \frac{\bar{U}_\mathrm{A} x_\mathrm{A} \Phi_{\mathrm{A}_1}}{\Phi_\mathrm{A}} \left(2 - r_\mathrm{A} r_\mathrm{B} K_\mathrm{AB}^2 \Phi_{\mathrm{A}_1} \Phi_{\mathrm{B}_1} U_\mathrm{A} U_\mathrm{B} \right) \\ & + \frac{\bar{U}_\mathrm{A} U_\mathrm{B} x_\mathrm{B} \Phi_{\mathrm{B}_1}}{U_\mathrm{A} \Phi_\mathrm{B}} \Bigg] + h_\mathrm{B} \Bigg[\frac{\bar{U}_\mathrm{B}}{K_\mathrm{AB} U_\mathrm{B}} \left(\frac{x_\mathrm{B}}{\Phi_\mathrm{B} r_\mathrm{A}} + \frac{x_\mathrm{A}}{\Phi_\mathrm{A} r_\mathrm{B}} \right) \\ & + \frac{\bar{U}_\mathrm{B} x_\mathrm{B} \Phi_{\mathrm{B}_1}}{\Phi_\mathrm{B}} \left(2 - r_\mathrm{A} r_\mathrm{B} K_\mathrm{AB}^2 \Phi_{\mathrm{A}_1} \Phi_{\mathrm{B}_1} U_\mathrm{A} U_\mathrm{B} \right) + \frac{U_\mathrm{A} \bar{U}_\mathrm{B} x_\mathrm{A} \Phi_{\mathrm{A}_1}}{U_\mathrm{B} \Phi_\mathrm{A}} \Bigg] \\ & + h_\mathrm{AB} \Bigg[\left(\frac{x_\mathrm{B}}{\Phi_\mathrm{B} r_\mathrm{A}} + \frac{x_\mathrm{A}}{\Phi_\mathrm{A} r_\mathrm{B}} \right) \frac{\left(1 + r_\mathrm{A} r_\mathrm{B} K_\mathrm{AB}^2 \Phi_{\mathrm{A}_1} \Phi_{\mathrm{B}_1} U_\mathrm{A} U_\mathrm{B} \right)}{K_\mathrm{AB}} \\ & + 2 \left(\frac{U_\mathrm{A} x_\mathrm{A} \Phi_{\mathrm{A}_1}}{\Phi_\mathrm{A}} + \frac{U_\mathrm{B} x_\mathrm{B} \Phi_{\mathrm{B}_1}}{\Phi_\mathrm{B}} \right) \Bigg] \Bigg\} \frac{r_\mathrm{A} r_\mathrm{B} K_\mathrm{AB}^2 \Phi_{\mathrm{A}_1} \Phi_{\mathrm{B}_1} U_\mathrm{A} U_\mathrm{B}}{\left(1 - r_\mathrm{A} r_\mathrm{B} K_\mathrm{AB}^2 \Phi_{\mathrm{A}_1} \Phi_{\mathrm{B}_1} U_\mathrm{A} U_\mathrm{B} \right)^2} \end{aligned} \tag{A17}$$

At pure alcohol states H_f reduces to H_fA^0 and H_fB^0, respectively.

$$H_\mathrm{fA}^0 = \frac{h_\mathrm{A} K_\mathrm{A} \Phi_{\mathrm{A}_1}^{02}}{\left(1 - K_\mathrm{A} \Phi_{\mathrm{A}_1}^0 \right)^2} = h_\mathrm{A} \bar{U}_\mathrm{A}^0 \Phi_{\mathrm{A}_1}^0 \tag{A18}$$

$$H_\mathrm{fB}^0 = \frac{h_\mathrm{B} K_\mathrm{B} \Phi_{\mathrm{B}_1}^{02}}{\left(1 - K_\mathrm{B} \Phi_{\mathrm{B}_1}^0 \right)^2} = h_\mathrm{B} \bar{U}_\mathrm{B}^0 \Phi_{\mathrm{B}_1}^0 \tag{A19}$$

The above equations are not equal to those based on an assumption of volume change of mixing [16].

REFERENCES

1 I. Nagata and K. Ohtsubo, Thermochim. Acta, 102 (1986) 267.
2 D.S. Abrams and J.M. Prausnitz, AIChE J., 21 (1975) 116.
3 V. Brandani, Fluid Phase Equilibria, 12 (1983) 87.
4 R.H. Stokes and C. Burfitt, J. Chem. Thermodyn., 5 (1973) 623.
5 J.H. Vera, S.G. Sayegh and G.A. Ratcliff, Fluid Phase Equilibria, 1 (1977) 113.
6 I. Nagata and K. Gotoh, Thermochim. Acta, 99 (1985) 145.
7 H.D. Pflug, A.E. Pope and G.C. Benson, J. Chem. Eng. Data, 13 (1968) 408.
8 M.I. Paz-Andrade, L. Romani and F. Gonzales, An. Quim., 70 (1974) 314.
9 H.H. Sun, J.J. Christensen, R.H. Izatt and R.W. Hanks, J. Chem. Thermodyn., 12 (1980) 95.
10 I. Nagata and K. Kazuma, J. Chem. Eng. Data, 22 (1977) 79.
11 R.S. Ramalho and M. Ruel, Can. J. Chem. Eng., 46 (1968) 456.
12 G. Geiseler, K. Quitzsch, J.H. Hesselbach and K. Schmidt, Z. Phys. Chem., Neue Folge, 60 (1968) 41.
13 M.K. Kumaran and G.C. Benson, J. Chem. Thermodyn., 16 (1984) 175.
14 R.S. Ramalho and M. Ruel, Can. J. Chem. Eng., 46 (1968) 467.
15 C. Pando, J.A.R. Renuncio, R.W. Hanks and J.J. Christensen, Ind. Eng. Chem., Process Des. Dev., 23 (1984) 73.
16 T. Hofman and I. Nagata, Chem. Eng. Sci., to be published.