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THERMODYNAMICS OF ALCOHOL SOLUTIONS. EXCESS MOLAR ENTHALPIES OF TERNARY MIXTURES CONTAINING TWO ALCOHOLS AND ONE ACTIVE NONASSOCIATING COMPONENT

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ABSTRACT

The UNIQUAC associated-solution theory proposed by Nagata and Gotoh to calculate the excess molar enthalpy of ternary mixtures containing two alcohols and one saturated hydrocarbon is extended to predict ternary excess molar enthalpies for mixtures formed by two alcohols and one active nonassociating component. The proposed model includes only binary parameters. Calculated results derived from the model are in excellent agreement with experimental excess molar enthalpies for ethanol–1-propanol–benzene at 25°C, measured with an isothermal dilution calorimeter.

INTRODUCTION

Studies on the thermodynamic properties of alcohol solutions are of great interest in this laboratory. Most of the measurements of excess molar enthalpy for ternary alcohol–hydrocarbon mixtures made in this laboratory are for mixtures including one alcohol and two hydrocarbons and chemical models were used for data analysis. Previous models were not suited for good representation of the behaviour of mixtures including two alcohols. The UNIQUAC associated-solution theory has been modified to overcome this disadvantage [1,2]. The newly proposed UNIQUAC associated-solution theory is well able to describe excess molar enthalpy data for binary alcohol–alcohol mixtures and to predict ternary excess molar enthalpies for mixtures formed by two alcohols and one saturated hydrocarbon from binary information alone without any ternary constants [2]. It is useful to extend the workability of the new UNIQUAC associated-solution theory to ternary mixtures including two alcohols and one active nonassociating component, where binary complex formation should be considered in all

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three binary combinations. A literature survey [3–5] shows that excess molar enthalpy data for these ternary solutions apparently seem not to exist.

In this paper, we present an extension of the UNIQUAC associated-solution theory to cover ternary systems formed by two alcohols and one active nonassociating component and the predictive ability of the proposed model is tested by comparing calculated results with experimental excess molar enthalpies for the ethanol–1-propanol–benzene system at 25°C, measured by an isothermal dilution calorimeter. Excess molar enthalpy data for all three component binary systems are available in the literature: for ethanol–1-propanol by Pflug et al. [6]; for ethanol–benzene and 1-propanol–benzene by Mrazek and Van Ness [7].

EXPERIMENTAL

C.P. alcohols were fractionally distilled in a glass column packed with McMahon packing after refluxing over calcium oxide. C.P. benzene was subjected to repeated recrystallization. Densities of purified chemicals, measured at 25°C with an Anton Paar (DMA-40) densimeter, agreed well the literature values [8]. An isothermal dilution calorimeter was used to measure the excess molar enthalpy of the ethanol–1-propanol–benzene system by adding benzene to an ethanol–1-propanol mixture of known composition. The experimental apparatus and procedure are the same as described previously [9].

RESULTS

The observed excess molar enthalpy H^E results are given in Table 1. The binary H^E results already have been fitted to polynomial equations [6,7]: eqn. (1) for ethanol–1-propanol; eqn. (2) for ethanol–benzene and 1-propanol–benzene.

$$H^E = x_1 x_2 \sum_{k=1}^{m} a_k (x_2 - x_1)^{k-1} \quad (1)$$

$$H^E = x_1 x_2 \cdot 10^4 / \sum_{k=1}^{m} a_k (x_2 - x_1)^{k-1} \quad (2)$$

The coefficients a_k of eqns. (1) and (2) are listed in Table 2. The ternary H^E results were correlated by eqns. (3) and (4).

$$H^E_{123} = H^E_{12} + H^E_{13} + H^E_{23} + x_1 x_2 x_3 \Delta_{123} \quad (3)$$

$$\Delta_{123}/RT = \sum_{i=1}^{m} b_i (1 - 2x_3)^{i-1} \quad (4)$$

TABLE 1

Experimental values of the excess molar enthalpies of ethanol(1)–1-propanol(2)–benzene(3) at 25°C [a]

$x_1' = 0.2509$			$x_1' = 0.5002$			$x_1' = 0.7501$		
x_1	x_2	H^E	x_1	x_2	H^E	x_1	x_2	H^E
0.2419	0.7222	81.7	0.4827	0.4824	81.5	0.7153	0.2380	93.5
0.2294	0.6848	178.8	0.4546	0.4542	184.1	0.6772	0.2257	179.9
0.2144	0.6401	297.2	0.4233	0.4230	300.7	0.6345	0.2144	279.7
0.1957	0.5841	443.7	0.3891	0.3888	427.8	0.5973	0.1990	367.0
0.1764	0.5266	585.1	0.3537	0.3534	554.9	0.5502	0.1833	475.8
0.1589	0.4745	705.6	0.3208	0.3206	662.3	0.4961	0.1653	592.0
0.1457	0.4351	786.0	0.2987	0.2985	727.7	0.4571	0.1523	668.6
0.1376	0.4109	830.9	0.2793	0.2791	780.2	0.4434	0.1478	693.4
0.1309	0.3908	864.1	0.2714	0.2712	799.1	0.4103	0.1367	749.9
0.1173	0.3501	920.2	0.2448	0.2446	858.5	0.3747	0.1249	803.4
0.1039	0.3103	961.2	0.2200	0.2198	902.1	0.3371	0.1123	848.9
0.0918	0.2742	983.9	0.1962	0.1961	931.7	0.3014	0.1004	881.8
0.0827	0.2470	990.0	0.1802	0.1801	943.8	0.2741	0.0913	897.3
0.0785	0.2342	989.4	0.1679	0.1678	948.3	0.2521	0.0840	904.8
0.0702	0.2095	981.4	0.1567	0.1574	948.3	0.2211	0.0737	905.6
0.0629	0.1878	966.5	0.1400	0.1406	943.2	0.1939	0.0646	895.2
0.0559	0.1670	944.9	0.1238	0.1243	928.5	0.1700	0.0566	876.2
0.0505	0.1509	921.9	0.1088	0.1093	905.6	0.1511	0.0504	854.1
0.0463	0.1382	900.0	0.0990	0.0995	885.4	0.1373	0.0458	834.0
0.0439	0.1309	886.6				0.1310	0.0436	822.6

[a] Values of H^E (in J mol^{-1}) were obtained by mixing pure benzene with $[(x_1')$ethanol + $(1-x_1')$1-propanol$]$.

where H_{12}^E is given by eqn. (1), H_{13}^E and H_{23}^E are calculated from eqn. (2), with the coefficients given in Table 2. An unweighted least-squares method gives the values of the coefficients of eqn. (4) and the standard deviation $\sigma(H^E)$: $b_1 = -2.2703$, $b_2 = 2.2011$, $b_3 = -1.5856$, $b_4 = 5.3698$, $b_5 = -13.6612$, $b_6 = 9.0092$ and $\sigma(H^E) = 4.6$ J mol^{-1} for ethanol–1-propanol–benzene.

TABLE 2

Coefficients a_k of eqns. (1) and (2)

System	a_1	a_2	a_3	a_4	a_5	a_6	Ref.
Ethanol–1-propanol	76.84	−10.62	8.81				6
Ethanol–benzene	3.2733	−2.1376	0.2546	−0.6895	−0.0321	−0.0388	7
1-Propanol–benzene	2.6287	−1.5119	0.2274	−0.5056	−0.1927	−0.0603	7

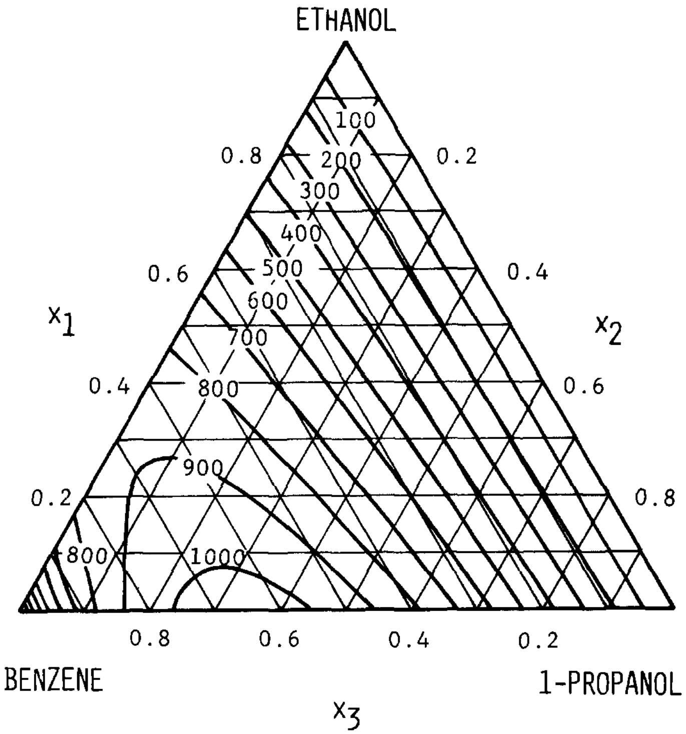

Fig. 1. Curves of constant H^{E} J mol^{-1} at 25°C for ethanol(1)–1-propanol(2)–benzene(3). The curves are calculated from eqn. (3).

Lines of constant values of H^{E} calculated from eqn. (3) are shown in Fig. 1.

THEORY

The UNIQUAC associated-solution theory is based on the basic assumptions that the equilibrium constants are independent of the degree of association and solvation and the structural parameters of complexes are expressed in terms of the corresponding units; for a simple complex A_iB_j formed by alcohols A and B, $r_{A_iB_j} = ir_A + jr_B$ and $q_{A_iB_j} = iq_A + jq_B$.

Binary alcohol–alcohol mixtures

The association constants of two alcohols A and B are defined by

$$K_A = \frac{\phi_{A_{i+1}}}{\phi_{A_i}\phi_{A_1}} \frac{i}{i+1} \tag{5}$$

$$K_B = \frac{\phi_{B_{i+1}}}{\phi_{B_i}\phi_{B_1}} \frac{i}{i+1} \tag{6}$$

According to various successive solvation reactions the solution contains multisolvated copolymers such as $(A_iB_j)_k$, $(B_iA_j)_k$, $A_i(B_jA_k)_l$ and $B_i(A_jB_k)_l$, where the suffixes i, j, k, and l go from one to infinity. A free hydroxyl group is attached to the tail molecule of these complexes. We use only a single value of the solvation constant K_{AB} for many consecutive reactions. For example, K_{AB} for $A_iB_j + A_k = A_iB_jA_k$ is defined by

$$K_{AB} = \frac{\phi_{A_iB_jA_k}}{\phi_{A_iB_j}\phi_{A_k}} \frac{r_{A_iB_j} r_{A_k}}{r_{A_iB_jA_k} r_A r_B} \tag{7}$$

The theory gives the excess molar enthalpy of the solution as the sum of a chemical and a physical contribution term.

$$H^E = H^E_{chem} + H^E_{phys} \tag{8}$$

The final expression of H^E_{chem} [2] is given by

$$\begin{aligned} H^E_{chem} = {} & h_A x_A \left(\frac{\bar{U}_A \phi_{A_1}}{\phi_A} - \bar{U}^0_A \phi^0_{A_1} \right) + h_B x_B \left(\frac{\bar{U}_B \phi_{B_1}}{\phi_B} - \bar{U}^0_B \phi^0_{B_1} \right) \\ & + \Bigg\{ h_A \Bigg[\frac{\bar{U}_A}{K_{AB} U_A} \left(\frac{x_B}{r_A \phi_B} + \frac{x_A}{r_B \phi_A} \right) + \frac{\bar{U}_A x_A \phi_{A_1}}{\phi_A} \\ & \qquad \times \left(2 - r_A r_B K^2_{AB} \phi_{A_1} \phi_{B_1} U_A U_B \right) + \frac{\bar{U}_A U_B x_B \phi_{B_1}}{U_A \phi_B} \Bigg] \\ & + h_B \Bigg[\frac{\bar{U}_B}{K_{AB} U_B} \left(\frac{x_B}{r_A \phi_B} + \frac{x_A}{r_B \phi_A} \right) + \frac{\bar{U}_B x_B \phi_{B_1}}{\phi_B} \\ & \qquad \times \left(2 - r_A r_B K^2_{AB} \phi_{A_1} \phi_{B_1} U_A U_B \right) + \frac{U_A \bar{U}_B x_A \phi_{A_1}}{U_B \phi_A} \Bigg] \\ & + h_{AB} \Bigg[\left(\frac{x_B}{r_A \phi_B} + \frac{x_A}{r_B \phi_A} \right) \frac{\left(1 + r_A r_B K^2_{AB} \phi_{A_1} \phi_{B_1} U_A U_B \right)}{K_{AB}} \\ & \qquad + 2 \left(\frac{U_A x_A \phi_{A_1}}{\phi_A} + \frac{U_B x_B \phi_{B_1}}{\phi_B} \right) \Bigg] \Bigg\} \\ & \times \frac{r_A r_B K^2_{AB} \phi_{A_1} \phi_{B_1} U_A U_B}{\left(1 - r_A r_B K^2_{AB} \phi_{A_1} \phi_{B_1} U_A U_B \right)^2} \end{aligned} \tag{9}$$

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

$$\bar{U}_A = K_A \phi_{A_1} / \left(1 - K_A \phi_{A_1} \right)^2 \tag{10}$$

$$U_A = 1 / \left(1 - K_A \phi_{A_1} \right) \tag{11}$$

$$\bar{U}_B = K_B \phi_{B_1} / \left(1 - K_B \phi_{B_1} \right)^2 \tag{12}$$

$$U_B = 1 / \left(1 - K_B \phi_{B_1} \right) \tag{13}$$

and the superscript ° denotes pure alcohol. The segment fractions of alcohol monomer, ϕ_{A_1} and ϕ_{B_1}, are simultaneously solved from mass balance equations given by

$$\phi_A = \bar{S}_A + \frac{r_A K_{AB} \bar{S}_A S_B}{\left(1 - r_A r_B K_{AB}^2 S_A S_B\right)^2}\left[2 + r_B K_{AB} S_A \left(2 - r_A r_B K_{AB}^2 S_A S_B\right) + r_A K_{AB} S_B\right] \tag{14}$$

$$\phi_B = \bar{S}_B + \frac{r_B K_{AB} S_A \bar{S}_B}{\left(1 - r_A r_B K_{AB}^2 S_A S_B\right)^2}\left[2 + r_A K_{AB} S_B \left(2 - r_A r_B K_{AB}^2 S_A S_B\right) + r_B K_{AB} S_A\right] \tag{15}$$

where $\bar{S}_A$, S_A, $\bar{S}_B$ and S_B are expressed in terms of the association constant and the segment fraction of alcohol monomer.

$$\bar{S}_A = \phi_{A_1} / \left(1 - K_A \phi_{A_1}\right)^2 \tag{16}$$

$$S_A = \phi_{A_1} / \left(1 - K_A \phi_{A_1}\right) \tag{17}$$

$$\bar{S}_B = \phi_{B_1} / \left(1 - K_B \phi_{B_1}\right)^2 \tag{18}$$

$$S_B = \phi_{B_1} / \left(1 - K_B \phi_{B_1}\right) \tag{19}$$

The segment fractions of alcohol monomer in pure alcohol states, $\phi_{A_1}^0$ and $\phi_{B_1}^0$ are given by

$$\phi_{A_1}^0 = \left[1 + 2K_A - (1 + 4K_A)^{1/2}\right] / 2K_A^2 \tag{20}$$

$$\phi_{B_1}^0 = \left[1 + 2K_B - (1 + 4K_B)^{1/2}\right] / 2K_B^2 \tag{21}$$

H_{phys}^E is also expressed by

$$H_{\text{phys}}^E = -R\left[\frac{q_A x_A \theta_B}{(\theta_A + \theta_B \tau_{BA})} \frac{\partial \tau_{BA}}{\partial(1/T)} + \frac{q_B x_B \theta_A}{(\theta_B + \theta_A \tau_{AB})} \frac{\partial \tau_{AB}}{\partial(1/T)}\right] \tag{22}$$

where the surface fractions, θ_A and θ_B, and two adjustable parameters, τ_{AB} and τ_{BA}, related to characteristic interaction parameters, are

$$\theta_A = x_A q_A / (x_A q_A + x_B q_B) \tag{23}$$

$$\theta_B = x_B q_B / (x_A q_A + x_B q_B) \tag{24}$$

$$\tau_{AB} = \exp(-a_{AB}/T) \tag{25}$$

$$\tau_{BA} = \exp(-a_{BA}/T) \tag{26}$$

As shown in data reduction, the physical contribution term was neglected for the ethanol–1-propanol system. This approximation is not justified if two alcohols are different appreciably in regard to their molecular structure.

Binary alcohol-active nonassociating component mixtures

The theory [10] assumes that alcohol A forms binary complexes A_iB with an active nonassociating component B according to the solvation reaction expressed by $A_i + B = A_iB$. The solvation constant K_{AB} is defined by

$$K_{AB} = \frac{\phi_{A_iB}}{\phi_{A_i}\phi_{B_1}} \frac{r_{A_i}}{r_{A_iB}r_A} \tag{27}$$

H^E_{chem} is described as

$$H^E_{chem} = h_A K_A x_A\left(\phi_{A_1} - \phi^0_{A_1}\right) + \frac{h_{AB} r_A K_{AB}\phi_{B_1} x_A\left(1 - K_A\phi_{A_1}\right)}{1 + r_A K_{AB}\phi_{B_1}} \tag{28}$$

ϕ_{A_1} and ϕ_{B_1} are obtained from the following mass balance equations

$$\phi_A = \frac{\phi_{A_1}}{\left(1 - K_A\phi_{A_1}\right)^2}\left[1 + r_A K_{AB}\phi_{B_1}\right] \tag{29}$$

$$\phi_B = \phi_{B_1}\left[1 + \frac{r_B K_{AB}\phi_{A_1}}{\left(1 - K_A\phi_{A_1}\right)}\right] \tag{30}$$

$\phi^0_{A_1}$ and H^E_{phys} are given by eqns. (20) and (22), respectively.

Ternary mixtures including two alcohols and one active nonassociating component

As follows A and B stand for two alcohols and C for an active nonassociating component. The theory further postulates that in addition to the binary complexes, ternary complexes are formed between alcohol copolymers and an active nonassociating component according to the following solvation reactions

$$\begin{aligned} &\left(A_iB_j\right)_k + C = \left(A_iB_j\right)_k C \\ &\left(B_iA_j\right)_k + C = \left(B_iA_j\right)_k C \\ &A_i\left(B_jA_k\right)_l + C = A_i\left(B_jA_k\right)_l C \\ &B_i\left(A_jB_k\right)_l + C = B_i\left(A_jB_k\right)_l C \end{aligned} \tag{31}$$

where the suffixes i, j, k, and l go from one to infinity. The excess molar enthalpy of the solution is the same as eqn. (8).

The definition of H^E_{chem} gives

$$H^E_{chem} = H_f - x_A H^0_{fA} - x_B H^0_{fB} \tag{32}$$

where H_f is the total enthalpy of complex formation in the solution and H^0_{fA}

and H^0_{fB} are the values of H_f at pure alcohol states, as shown in the Appendix.

Substitution of H_f, H^0_{fA} and H^0_{fB} into eqn. (32) yields

$$H^E_{chem} = h_A x_A \left(\frac{\overline{U}_A \phi_{A_1}}{\phi_A} - \overline{U}^0_A \phi^0_{A_1} \right) + h_B x_B \left(\frac{\overline{U}_B \phi_{B_1}}{\phi_B} - \overline{U}^0_B \phi^0_{B_1} \right)$$

$$+ (h_A \overline{U}_A + h_{AC} U_A) \frac{r_A K_{AC} \phi_{C_1} x_A \phi_{A_1}}{\phi_A} + (h_B \overline{U}_B + h_{BC} U_B) \frac{r_B K_{BC} \phi_{C_1} x_B \phi_{B_1}}{\phi_B}$$

$$+ \left(h_A \left\{ \frac{\overline{U}_A}{K_{AB} U_A} \left(\frac{x_B}{r_A \phi_B} + \frac{x_A}{r_B \phi_A} \right) + \frac{\overline{U}_A x_A \phi_{A_1}}{\phi_A} \right. \right.$$

$$\left(2 - r_A r_B K^2_{AB} \phi_{A_1} \phi_{B_1} U_A U_B \right) + \frac{\overline{U}_A U_B x_B \phi_{B_1}}{U_A \phi_B}$$

$$+ \phi_{C_1} \left[\left(\frac{r_B K_{BC} x_B}{r_A K_{AB} \phi_B} + \frac{r_A K_{AC} x_A}{r_B K_{AB} \phi_A} \right) \frac{\overline{U}_A}{U_A} + \frac{r_A K_{AC} \overline{U}_A x_A \phi_{A_1}}{\phi_A} \right.$$

$$\left. \left. \times \left(2 - r_A r_B K^2_{AB} \phi_{A_1} \phi_{B_1} U_A U_B \right) + \frac{r_B K_{BC} \overline{U}_A U_B x_B \phi_{B_1}}{U_A \phi_B} \right] \right\}$$

$$+ h_B \left\{ \frac{\overline{U}_B}{K_{AB} U_B} \left(\frac{x_B}{r_A \phi_B} + \frac{x_A}{r_B \phi_A} \right) + \frac{\overline{U}_B x_B \phi_{B_1}}{\phi_B} \right.$$

$$\times \left(2 - r_A r_B K^2_{AB} \phi_{A_1} \phi_{B_1} U_A U_B \right) + \frac{U_A \overline{U}_B x_A \phi_{A_1}}{U_B \phi_A}$$

$$+ \phi_{C_1} \left[\left(\frac{r_B K_{BC} x_B}{r_A K_{AB} \phi_B} + \frac{r_A K_{AC} x_A}{r_B K_{AB} \phi_A} \right) \frac{\overline{U}_B}{U_B} + \frac{r_B K_{BC} \overline{U}_B x_B \phi_{B_1}}{\phi_B} \right.$$

$$\left. \left. \times \left(2 - r_A r_B K^2_{AB} \phi_{A_1} \phi_{B_1} U_A U_B \right) + \frac{r_A K_{AC} \overline{U}_B U_A x_A \phi_{A_1}}{U_B \phi_A} \right] \right\}$$

$$+ h_{AB} \left\{ \left(\frac{x_B}{r_A \phi_B} + \frac{x_A}{r_B \phi_A} \right) \frac{\left(1 + r_A r_B K^2_{AB} \phi_{A_1} \phi_{B_1} U_A U_B \right)}{K_{AB}} \right.$$

$$+ 2 \left(\frac{U_A x_A \phi_{A_1}}{\phi_A} + \frac{U_B x_B \phi_{B_1}}{\phi_B} \right)$$

$$+ \phi_{C_1} \left[\left(\frac{r_B K_{BC} x_B}{r_A \phi_B} + \frac{r_A K_{AC} x_A}{r_B \phi_A} \right) \frac{\left(1 + r_A r_B K^2_{AB} \phi_{A_1} \phi_{B_1} U_A U_B \right)}{K_{AB}} \right.$$

$$\left. \left. + 2 \left(\frac{r_A K_{AC} U_A x_A \phi_{A_1}}{\phi_A} + \frac{r_B K_{BC} U_B x_B \phi_{B_1}}{\phi_B} \right) \right] \right\}$$

$$+\left[h_{AC} r_A K_{AC} \phi_{C_1}\left(\frac{U_A x_A \phi_{A_1}}{\phi_A} + \frac{x_A}{r_A K_{AB} \phi_A}\right) + h_{BC} r_B K_{BC} \phi_{C_1} \times\left(\frac{U_B x_B \phi_{B_1}}{\phi_B} + \frac{x_B}{r_A K_{AB} \phi_B}\right)\right]$$

$$\times\left(1 - r_A r_B K_{AB}^2 \phi_{A_1} \phi_{B_1} U_A U_B\right)\Bigg) \frac{r_A r_B K_{AB}^2 \phi_{A_1} \phi_{B_1} U_A U_B}{\left(1 - r_A r_B K_{AB}^2 \phi_{A_1} \phi_{B_1} U_A U_B\right)^2} \quad (33)$$

where $\bar{U}_A$, U_A, $\bar{U}_B$ and U_B are given by eqns. (10)–(13), respectively.

The segment fractions of the component monomer are obtained by simultaneous solution of the following mass balance equations [1]

$$\phi_A = \left(1 + r_A K_{AC} \phi_{C_1}\right)\bar{S}_A + \frac{r_A K_{AB} \bar{S}_A S_B}{\left(1 - r_A r_B K_{AB}^2 S_A S_B\right)^2} \times\Big\{2 + r_B K_{AB} S_A\left(2 - r_A r_B K_{AB}^2 S_A S_B\right) + r_A K_{AB} S_B + \phi_{C_1}\left[\left(r_A K_{AC} + r_B K_{BC}\right) + r_A r_B K_{AB} K_{AC} S_A\left(2 - r_A r_B K_{AB}^2 S_A S_B\right) + r_A r_B K_{AB} K_{BC} S_B\right]\Big\} \quad (34)$$

$$\phi_B = \left(1 + r_B K_{BC} \phi_{C_1}\right)\bar{S}_B + \frac{r_B K_{AB} S_A \bar{S}_B}{\left(1 - r_A r_B K_{AB}^2 S_A S_B\right)^2} \times\Big\{2 + r_A K_{AB} S_B\left(2 - r_A r_B K_{AB}^2 S_A S_B\right) + r_B K_{AB} S_A + \phi_{C_1}\left[\left(r_A K_{AC} + r_B K_{BC}\right) + r_A r_B K_{AB} K_{BC} S_B\left(2 - r_A r_B K_{AB}^2 S_A S_B\right) + r_A r_B K_{AB} K_{AC} S_A\right]\Big\} \quad (35)$$

$$\phi_C = \phi_{C_1}\left\{1 + r_C K_{AC} S_A + r_C K_{BC} S_B + \frac{r_A r_B r_C K_{AB}^2 S_A S_B}{\left(1 - r_A r_B K_{AB}^2 S_A S_B\right)} \times\left[\frac{K_{AC}}{r_B K_{AB}} + \frac{K_{BC}}{r_A K_{AB}} + K_{AC} S_A + K_{BC} S_B\right]\right\} \quad (36)$$

where $\bar{S}_A$, S_A, $\bar{S}_B$ and S_B are defined by eqns. (16)–(19), respectively.

H_{phys}^E [2] is written as

$$H_{phys}^E = -R \sum_I q_I x_I \frac{\sum_J \theta_J \dfrac{\partial \tau_{JI}}{\partial(1/T)}}{\sum_J \theta_J \tau_{JI}} \quad (37)$$

where θ_I and τ_{JI} are given by

$$\theta_I = q_I x_I / \sum_J q_J x_J \tag{38}$$

$$\tau_{JI} = \exp(-a_{JI}/T) \tag{39}$$

and the temperature dependence of a_{JI} is approximated by a linear function of temperature expressed as

$$a_{JI} = C_I + D_I(T - 273.15) \tag{40}$$

CALCULATED RESULTS

The association constants of pure alcohols at 50°C were taken from Brandani [11] and the enthalpy of a hydrogen bond was set as −23.2 kJ mol^{-1}, which is the enthalpy of dilution of ethanol in n-hexane at 25°C [12]. Table 3 lists the solvation constants and enthalpies of complex formation for the three binary systems [2,13]. The temperature dependence of the equilibrium constants is expressed by the van't Hoff relation. The values of the enthalpy of a hydrogen bond and all the enthalpies of solvation were assumed to be independent of temperature. The pure component structural parameters were calculated in accordance with the method of Vera et al. [14]. Table 4 shows the binary calculated results and the calculated results

TABLE 3

Values of solvation constants and enthalpies of complex formation

System	K_{AB} at 50°C	$-h_{AB}$ (kJ mol^{-1})
Ethanol–1-propanol	49.0	23.2
Ethanol–benzene	3.0	8.3
1-propanol–benzene	2.5	8.3

TABLE 4

Results obtained in fitting the UNIQUAC associated-solution theory to excess molar enthalpies at 25°C

System(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	2.1	0.0	0.0	0.0	0.0	6
Ethanol–benzene	10	3.2	952.39	−26.58	2.2553	0.1347	7
1-Propanol–benzene	10	5.7	807.50	355.03	2.0554	1.3727	7

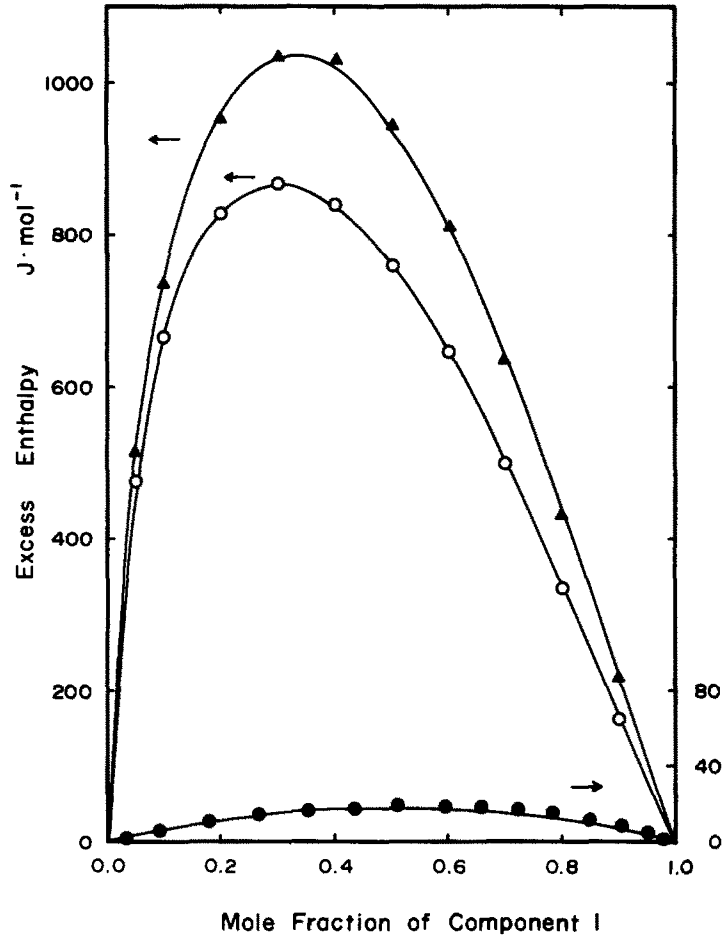

Fig. 2. Excess molar enthalpies at 25°C for binary mixtures. Experimental: (●) ethanol(1)–1-propanol(2), data of Pflug et al. [6]; (○) ethanol(1)–benzene(2), data of Mrazek and Van Ness [7]; (▲) 1-propanol(1)–benzene(2), data of Mrazek and Van Ness [7]. (———) Calculated from the UNIQUAC associated-solution theory.

are compared with the experimental data in Fig. 2. The absolute arithmetic mean deviation between the 59 experimental and calculated excess molar enthalpy data points is 7.01 J mol^{-1} and the absolute percentage mean deviation is 1.66%.

We conclude that the UNIQUAC associated-solution theory gives a good prediction of the excess molar enthalpy of concentration solution formed by ethanol, 1-propanol and benzene, because the overall mean deviation for the 18 ternary systems including two alcohols and one saturated hydrocarbon is 10.79 J mol^{-1} [2].

LIST OF SYMBOLS

A, B, C	alcohols and active nonassociating component
A_1, A_i	monomer and i-mer of alcohol A
A_iB_j	complex composed of i-mer of alcohol A and j-mer of alcohol B
A_iC	complex composed of i-mer of alcohol A and one molecule of component C
a_{IJ}	binary interaction parameter
a_k	coefficient of eqns. (1) and (2)
B_1, B_i	monomer and i-mer of alcohol B
B_iC	complex composed of i-mer of alcohol B and one molecule of component C
b_k	coefficient of eqn. (4)
C_I, D_I	coefficients of eqn. (40)
H_f	total enthalpy of complex formation
H^E	molar excess enthalpy
h_A, h_B	enthalpies of hydrogen bond formation
h_{AB}, h_{AC}, h_{BC}	enthalpies of complex formation between unlike molecules
K_A, K_B	association constants for pure alcohols A and B
K_{AB}, K_{AC}, K_{BC}	solvation constants between unlike molecules
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
$\bar{S}_A$, $\bar{S}_B$	sums as defined by eqns. (16) and (18)
S_A, S_B	sums as defined by eqns. (17) and (19)
T	absolute temperature
$\bar{U}_A$, $\bar{U}_B$	quantities as defined by eqns. (10) and (12)
U_A, U_B	quantities as defined by eqns. (11) and (13)
x	liquid-phase mole fraction

Greek letters

Δ_{123}	function as defined by eqn. (4)
θ_I	surface fraction of component I
τ_{IJ}	coefficient as defined by $\exp(-a_{IJ}/T)$
σ	standard deviation
ϕ_I	segment fraction of component I
ϕ_{I_1}	segment fraction of monomeric 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, AC, BC	binary complexes
A_iB_j	complex composed of *i*-mer of alcohol A and *j*-mer of alcohol B
A_iB_jC	complex composed of *i*-mer of alcohol A, *j*-mer of alcohol B and one molecule of component C
A_iC	complex composed of *i*-mer of alcohol A and one molecule of component C
B_iC	complex composed of *i*-mer of alcohol B and one molecule of component C
chem	chemical
f	complex formation
I, *J*	components
i, *j*, *k*, *l*, *m*, *n*, *o*	*i*, *j*, *k*, *l*, *m*, *n* and *o*-mers of alcohols or suffixes
phys	physical

Superscript

0	pure alcohol reference state

APPENDIX

In one mole of the ternary solution containing two alcohols and one active nonassociating component, alcohols self-associate and solvate to form pure *i*-mers, A_i and B_i, and multisolvated copolymers, $(A_iB_j)_k$, $A_i(B_jA_k)_l$, $(B_iA_j)_k$ and $B_i(A_jB_k)_l$, where the suffixes *i*, *j*, *k* and *l* go from one to infinity, and these alcohol polymers form ternary complexes, $(A_iB_j)_kC$, $A_i(B_jA_k)_lC$, $(B_iA_j)_kC$ and $B_i(A_jB_k)_lC$, with an active nonassociating component.

The total enthalpy of complex formation in the solution is expressed by

$$H_f = h_A\Big\{\sum_i (i-1)n_{A_i} + \sum_i\sum_j (i-1)n_{A_iB_j} + \sum_i\sum_j\sum_k [(i-1)+(k-1)]\,n_{A_iB_jA_k}$$
$$+\sum_i\sum_j\sum_k\sum_l [(i-1)+(k-1)]\,n_{A_iB_jA_kB_l} + \ldots$$
$$+\sum_i\sum_j (j-1)n_{B_iA_j} + \sum_i\sum_j\sum_k (j-1)n_{B_iA_jB_k}$$
$$+\sum_i\sum_j\sum_k\sum_l [(j-1)+(l-1)]\,n_{B_iA_jB_kA_l} + \ldots$$

$$+\sum_i (i-1)n_{A_iC} + \sum_i\sum_j (i-1)n_{A_iB_jC}$$

$$+\sum_i\sum_j\sum_k [(i-1)+(k-1)]\,n_{A_iB_jA_kC}$$

$$+\sum_i\sum_j\sum_k\sum_l [(i-1)+(k-1)]\,n_{A_iB_jA_kB_lC} + \cdots$$

$$+\sum_i\sum_j (j-1)n_{B_iA_jC} + \sum_i\sum_j\sum_k (j-1)n_{B_iA_jB_kC}$$

$$+\sum_i\sum_j\sum_k\sum_l [(j-1)+(l-1)]\,n_{B_iA_jB_kA_lC} + \cdots\Big\}$$

$$+h_B\Big\{\sum_i (i-1)n_{B_i} + \sum_i\sum_j (i-1)n_{B_iA_j}$$

$$+\sum_i\sum_j\sum_k [(i-1)+(k-1)]\,n_{B_iA_jB_k}$$

$$+\sum_i\sum_j\sum_k\sum_l [(i-1)+(k-1)]\,n_{B_iA_jB_kA_l} + \cdots$$

$$+\sum_i\sum_j (j-1)n_{A_iB_j} + \sum_i\sum_j\sum_k (j-1)n_{A_iB_jA_k}$$

$$+\sum_i\sum_j\sum_k\sum_l [(j-1)+(l-1)]\,n_{A_iB_jA_kB_l} + \cdots$$

$$+\sum_i (i-1)n_{B_iC} + \sum_i\sum_j (i-1)n_{B_iA_jC}$$

$$+\sum_i\sum_j\sum_k [(i-1)+(k-1)]\,n_{B_iA_jB_kC}$$

$$+\sum_i\sum_j\sum_k\sum_l [(i-1)+(k-1)]\,n_{B_iA_jB_kA_lC} + \cdots$$

$$+\sum_i\sum_j (j-1)n_{A_iB_jC} + \sum_i\sum_j\sum_k (j-1)n_{A_iB_jA_kC}$$

$$+\sum_i\sum_j\sum_k\sum_l [(j-1)+(l-1)]\,n_{A_iB_jA_kB_lC} + \cdots\Big\}$$

$$+h_{AB}\Big\{\sum_i\sum_j n_{A_iB_j} + 2\sum_i\sum_j\sum_k n_{A_iB_jA_k} + 3\sum_i\sum_j\sum_k\sum_l n_{A_iB_jA_kB_l}$$

$$+4\sum_i\sum_j\sum_k\sum_l\sum_m n_{A_iB_jA_kB_lA_m} + \cdots$$

$$+\sum_i\sum_j n_{B_iA_j} + 2\sum_i\sum_j\sum_k n_{B_iA_jB_k} + 3\sum_i\sum_j\sum_k\sum_l n_{B_iA_jB_kA_l}$$

$$+4\sum_i\sum_j\sum_k\sum_l\sum_m n_{B_iA_jB_kA_lB_m} + \cdots$$

$$+\sum_i\sum_j n_{A_iB_jC}+2\sum_i\sum_j\sum_k n_{A_iB_jA_kC}+3\sum_i\sum_j\sum_k\sum_l n_{A_iB_jA_kB_lC}$$

$$+4\sum_i\sum_j\sum_k\sum_l\sum_m n_{A_iB_jA_kB_lA_mC}+\dots$$

$$+\sum_i\sum_j n_{B_iA_jC}+2\sum_i\sum_j\sum_k n_{B_iA_jB_kC}+3\sum_i\sum_j\sum_k\sum_l n_{B_iA_jB_kA_lC}$$

$$+4\sum_i\sum_j\sum_k\sum_l\sum_l\sum_m n_{B_iA_jB_kA_lB_mC}+\dots\Big\}$$

$$+h_{AC}\Big\{\sum_i n_{A_iC}+\sum_i\sum_j\sum_k n_{A_iB_jA_kC}+\sum_i\sum_j\sum_k\sum_l\sum_m n_{A_iB_jA_kB_lA_mC}$$

$$+\sum_i\sum_j\sum_k\sum_l\sum_m\sum_n\sum_o n_{A_iB_jA_kB_lA_mB_nA_oC}+\dots$$

$$+\sum_i\sum_j n_{B_iA_jC}+\sum_i\sum_j\sum_k\sum_l n_{B_iA_jB_kA_lC}$$

$$+\sum_i\sum_j\sum_k\sum_l\sum_m\sum_n n_{B_iA_jB_kA_lB_mA_nC}+\dots\Big\}$$

$$+h_{BC}\Big\{\sum n_{B_iC}+\sum_i\sum_j\sum_k n_{B_iA_jB_kC}+\sum_i\sum_j\sum_k\sum_l\sum_m n_{B_iA_jB_kA_lB_mC}$$

$$+\sum_i\sum_j\sum_k\sum_l\sum_m\sum_n\sum_o n_{B_iA_jB_kA_lB_mA_nB_oC}+\dots$$

$$+\sum_i\sum_j n_{A_iB_jC}+\sum_i\sum_j\sum_k\sum_l n_{A_iB_jA_kB_lC}$$

$$+\sum_i\sum_j\sum_k\sum_l\sum_m\sum_n n_{A_iB_jA_kB_lA_mB_nC}+\dots\Big\} \tag{A1}$$

where $\sum_i$ denotes $\sum_{i=1}^{\infty}$. H_f can be also written as

$$H_f=h_A(S_1+S_2+S_3+S_4)+h_B(S_5+S_6+S_7+S_8)$$
$$+h_{AB}(S_9+S_{10})+h_{AC}(S_{11}+S_{12})+h_{BC}(S_{13}+S_{14}) \tag{A2}$$

where S_1, S_2, S_5, S_6 and S_9 have been already derived in the previous paper [2].

$$S_1=\sum_i(i-1)n_{A_i}=\frac{K_A\phi_{A_1}n_{A_1}}{(1-K_A\phi_{A_1})^2}=\overline{U}_An_{A_1} \tag{A3}$$

$$S_2=\sum_i\sum_j(i-1)n_{A_iB_j}+\sum_i\sum_j\sum_k[(i-1)+(k-1)]n_{A_iB_jA_k}$$
$$+\sum_i\sum_j\sum_k\sum_l[(i-1)+(k-1)]n_{A_iB_jA_kB_l}$$

$$+\sum_i\sum_j\sum_k\sum_l\sum_m[(i-1)+(k-1)+(m-1)]\,n_{A_iB_jA_kB_lA_m}+\cdots$$

$$+\sum_i\sum_j(j-1)n_{B_iA_j}+\sum_i\sum_j\sum_k(j-1)n_{B_iA_jB_k}$$

$$+\sum_i\sum_j\sum_k\sum_l[(j-1)+(l-1)]\,n_{B_iA_jB_kA_l}$$

$$+\sum_i\sum_j\sum_k\sum_l\sum_m[(j-1)+(l-1)]\,n_{B_iA_jB_kA_lB_m}+\cdots$$

$$=\left[\frac{\overline{U}_A}{K_{AB}U_A}\left(\frac{n_{B_1}}{r_A\phi_{B_1}}+\frac{n_{A_1}}{r_B\phi_{A_1}}\right)+\overline{U}_A n_{A_1}\left(2-r_Ar_BK_{AB}^2\phi_{A_1}\phi_{B_1}U_AU_B\right)\right.$$

$$\left.+\frac{\overline{U}_AU_Bn_{B_1}}{U_A}\right]\frac{r_Ar_BK_{AB}^2\phi_{A_1}\phi_{B_1}U_AU_B}{\left(1-r_Ar_BK_{AB}^2\phi_{A_1}\phi_{B_1}U_AU_B\right)^2} \quad \text{(A4)}$$

$$S_3=\sum_i(i-1)n_{A_iC}=\frac{K'_{AC}\phi_{C_1}n_{A_1}}{r_C}\sum_i(i-1)\left(K_A\phi_{A_1}\right)^{i-1}$$

$$=\frac{K'_{AC}\phi_{C_1}K_A\phi_{A_1}n_{A_1}}{r_C\left(1-K_A\phi_{A_1}\right)^2}=r_AK_{AC}\phi_{C_1}\overline{U}_An_{A_1} \quad \text{(A5)}$$

$$S_4=\sum_i\sum_j(i-1)n_{A_iB_jC}+\sum_i\sum_j\sum_k[(i-1)+(k-1)]\,n_{A_iB_jA_kC}$$

$$+\sum_i\sum_j\sum_k\sum_l[(i-1)+(k-1)]\,n_{A_iB_jA_kB_lC}$$

$$+\sum_i\sum_j\sum_k\sum_l\sum_m[(i-1)+(k-1)+(m-1)]\,n_{A_iB_jA_kB_lA_mC}+\cdots$$

$$+\sum_i\sum_j(j-1)n_{B_iA_jC}+\sum_i\sum_j\sum_k(j-1)n_{B_iA_jB_kC}$$

$$+\sum_i\sum_j\sum_k\sum_l[(j-1)+(l-1)]\,n_{B_iA_jB_kA_lC}$$

$$+\sum_i\sum_j\sum_k\sum_l\sum_m[(j-1)+(l-1)]\,n_{B_iA_jB_kA_lB_mC}+\cdots$$

$$=\frac{K'_{BC}\phi_{C_1}K'_{AB}}{r_CV}\sum_i(i-1)n_{A_i}\sum_j n_{B_j}+\frac{K'_{AC}\phi_{C_1}K'^2_{AB}}{r_CV^2}$$

$$\times\left[\sum_i(i-1)n_{A_i}\sum_j n_{B_j}\sum_k n_{A_k}+\sum_i n_{A_i}\sum_j n_{B_j}\sum_k(k-1)n_{A_k}\right]$$

$$+\frac{K'_{BC}\phi_{C_1}K'^3_{AB}}{r_C V^3}\left[\sum_i (i-1)n_{A_i}\sum_j n_{B_j}\sum_k n_{A_k}\sum_l n_{B_l}\right.$$

$$\left.+\sum_i n_{A_i}\sum_j n_{B_j}\sum_k (k-1)n_{A_k}\sum_l n_{B_l}\right]+\ldots$$

$$+\frac{K'_{AC}\phi_{C_1}K'_{AB}}{r_C V}\sum_i n_{B_i}\sum_j (j-1)n_{A_j}+\frac{K'_{BC}\phi_{C_1}K'^2_{AB}}{r_C V^2}\sum_i n_{B_i}$$

$$\times\sum_j (j-1)n_{A_j}\sum_k n_{B_k}$$

$$+\frac{K'_{AC}\phi_{C_1}K'^3_{AB}}{r_C V^3}\left[\sum_i n_{B_i}\sum_j (j-1)n_{A_j}\sum_k n_{B_k}\sum_l n_{A_l}\right.$$

$$\left.+\sum_i n_{B_i}\sum_j n_{A_j}\sum_k n_{B_k}\sum_l (l-1)n_{A_l}\right]+\ldots$$

$$=\frac{K'_{BC}\phi_{C_1}K'_{AB}}{r_C V}\overline{U}_A n_{A_1}U_B n_{B_1}+\frac{2K'_{AC}\phi_{C_1}K'^2_{AB}}{r_C V^2}\overline{U}_A n_{A_1}U_B n_{B_1}U_A n_{A_1}$$

$$+\frac{2K'_{BC}\phi_{C_1}K'^3_{AB}}{r_C V^3}\overline{U}_A n_{A_1}U_B n_{B_1}U_A n_{A_1}U_B n_{B_1}$$

$$+\frac{3K'_{AC}\phi_{C_1}K'^4_{AB}}{r_C V^4}\overline{U}_A n_{A_1}U_B n_{B_1}U_A n_{A_1}U_B n_{B_1}U_A n_{A_1}+\ldots$$

$$+\frac{K'_{AC}\phi_{C_1}K'_{AB}}{r_C V}U_B n_{B_1}\overline{U}_A n_{A_1}+\frac{K'_{BC}\phi_{C_1}K'^2_{AB}}{r_C V^2}U_B n_{B_1}\overline{U}_A n_{A_1}U_B n_{B_1}$$

$$+\frac{2K'_{AC}\phi_{C_1}K'^3_{AB}}{r_C V^3}U_B n_{B_1}\overline{U}_A n_{A_1}U_B n_{B_1}U_A n_{A_1}$$

$$+\frac{2K'_{BC}\phi_{C_1}K'^4_{AB}}{r_C V^4}U_B n_{B_1}\overline{U}_A n_{A_1}U_B n_{B_1}U_A n_{A_1}U_B n_{B_1}+\ldots$$

$$=r_B^2K_{BC}K_{AB}\phi_{C_1}\phi_{A_1}n_{B_1}\overline{U}_A U_B+2r_A K_{AC}\phi_{C_1}\overline{U}_A n_{A_1}\left(r_A r_B K^2_{AB}\phi_{A_1}\phi_{B_1}U_A U_B\right)$$

$$+2r_B^2K_{BC}K_{AB}\phi_{C_1}\phi_{A_1}n_{B_1}\overline{U}_A U_B\left(r_A r_B K^2_{AB}\phi_{A_1}\phi_{B_1}U_A U_B\right)$$

$$+3r_A K_{AC}\phi_{C_1}\overline{U}_A n_{A_1}\left(r_A r_B K^2_{AB}\phi_{A_1}\phi_{B_1}U_A U_B\right)^2+\ldots$$

$$
\begin{aligned}
&+r_A^2 K_{AC} K_{AB} \phi_{C_1} \phi_{B_1} n_{A_1} \bar{U}_A U_B \\
&+r_B K_{BC} \phi_{C_1} (\bar{U}_A / U_A) U_B n_{B_1} \left(r_A r_B K_{AB}^2 \phi_{A_1} \phi_{B_1} U_A U_B \right) \\
&+2 r_A^2 K_{AC} K_{AB} \phi_{C_1} \phi_{B_1} n_{A_1} \bar{U}_A U_B \left(r_A r_B K_{AB}^2 \phi_{A_1} \phi_{B_1} U_A U_B \right) \\
&+2 r_B K_{AB} \phi_{C_1} (\bar{U}_A / U_A) U_B n_{B_1} \left(r_A r_B K_{AB}^2 \phi_{A_1} \phi_{B_1} U_A U_B \right)^2 \\
&+ \dots \\
= &\, r_B^2 K_{BC} K_{AB} \phi_{C_1} \phi_{A_1} n_{B_1} \bar{U}_A U_B \sum_i i \left(r_A r_B K_{AB}^2 \phi_{A_1} \phi_{B_1} U_A U_B \right)^{i-1} \\
&+ r_A K_{AC} \phi_{C_1} \bar{U}_A n_{A_1} \sum_i (i+1) \left(r_A r_B K_{AB}^2 \phi_{A_1} \phi_{B_1} U_A U_B \right)^i \\
&+ r_A^2 K_{AC} K_{AB} \phi_{C_1} \phi_{B_1} n_{A_1} \bar{U}_A U_B \sum_i i \left(r_A r_B K_{AB}^2 \phi_{A_1} \phi_{B_1} U_A U_B \right)^{i-1} \\
&+ \frac{r_B K_{BC} \phi_{C_1} \bar{U}_A U_B n_{B_1}}{U_A} \sum_i i \left(r_A r_B K_{AB}^2 \phi_{A_1} \phi_{B_1} U_A U_B \right)^i \\
= &\, \phi_{C_1} \left[\left(\frac{r_B K_{BC} n_{B_1}}{r_A K_{AB} \phi_{B_1}} + \frac{r_A K_{AC} n_{A_1}}{r_B K_{AB} \phi_{A_1}} \right) \frac{\bar{U}_A}{U_A} + r_A K_{AC} \bar{U}_A n_{A_1} \right. \\
&\quad \times \left(2 - r_A r_B K_{AB}^2 \phi_{A_1} \phi_{B_1} U_A U_B \right) \\
&\quad \left. + \frac{r_B K_{BC} \bar{U}_A U_B n_{B_1}}{U_A} \right] \frac{r_A r_B K_{AB}^2 \phi_{A_1} \phi_{B_1} U_A U_B}{\left(1 - r_A r_B K_{AB}^2 \phi_{A_1} \phi_{B_1} U_A U_B \right)^2}
\end{aligned}
\tag{A6}
$$

where $K'_{AB} = r_A r_B K_{AB}$, $K'_{AC} = r_A r_C K_{AC}$, $K'_{BC} = r_B r_C K_{BC}$ and V is the true molar volume of the solution.

$$
S_5 = \sum_i (i-1) n_{B_i} = \frac{K_B \phi_{B_1} n_{B_1}}{\left(1 - K_B \phi_{B_1}\right)^2} = \bar{U}_B n_{B_1} \tag{A7}
$$

$$
\begin{aligned}
S_6 = &\sum_i \sum_j (i-1) n_{B_i A_j} + \sum_i \sum_j \sum_k [(i-1) + (k-1)] n_{B_i A_j B_k} \\
&+ \sum_i \sum_j \sum_k \sum_l [(i-1) + (k-1)] n_{B_i A_j B_k A_l} + \dots \\
&+ \sum_i \sum_j (j-1) n_{A_i B_j} + \sum_i \sum_j \sum_k (j-1) n_{A_i B_j A_k} \\
&+ \sum_i \sum_j \sum_k \sum_l [(j-1) + (l-1)] n_{A_i B_j A_k B_l} + \dots
\end{aligned}
$$

$$= \left[\frac{\overline{U}_{B}}{K_{AB}U_{B}} \left(\frac{n_{B_1}}{r_A \phi_{B_1}} + \frac{n_{A_1}}{r_B \phi_{A_1}} \right) + \overline{U}_B n_{B_1} \right.$$

$$\left. \times \left(2 - r_A r_B K_{AB}^2 \phi_{A_1} \phi_{B_1} U_A U_B\right) + \frac{\overline{U}_B U_A n_{A_1}}{U_B} \right]$$

$$\times \frac{r_A r_B K_{AB}^2 \phi_{A_1} \phi_{B_1} U_A U_B}{\left(1 - r_A r_B K_{AB}^2 \phi_{A_1} \phi_{B_1} U_A U_B\right)^2} \tag{A8}$$

$$S_7 = \sum_i (i-1) n_{B_i C} = \frac{K'_{BC} \phi_{C_1} K_B \phi_{B_1} n_{B_1}}{r_C \left(1 - K_B \phi_{B_1}\right)^2} = r_B K_{BC} \phi_{C_1} \overline{U}_B n_{B_1} \tag{A9}$$

In the same way as described for S_4, we can obtain

$$S_8 = \sum_i \sum_j (i-1) n_{B_i A_j C} + \sum_i \sum_j \sum_k [(i-1) + (k-1)] n_{B_i A_j B_k C}$$

$$+ \sum_i \sum_j \sum_k \sum_l [(i-1) + (k-1)] n_{B_i A_j B_k A_l C} + \dots$$

$$+ \sum_i \sum_j (j-1) n_{A_i B_j C} + \sum_i \sum_j \sum_k (j-1) n_{A_i B_j A_k C}$$

$$+ \sum_i \sum_j \sum_k \sum_l [(i-1) + (l-1)] n_{A_i B_j A_k B_l C} + \dots$$

$$= \phi_{C_1} \left[\left(\frac{r_B K_{BC} n_{B_1}}{r_A K_{AB} \phi_B} + \frac{r_A K_{AC} n_{A_1}}{r_B K_{AB} \phi_A} \right) \frac{\overline{U}_B}{U_B} + r_B K_{BC} \overline{U}_B n_{B_1} \right.$$

$$\times \left(2 - r_A r_B K_{AB}^2 \phi_{A_1} \phi_{B_1} U_A U_B\right)$$

$$\left. + \frac{r_A K_{AC} \overline{U}_B U_A n_{A_1}}{U_B} \right] \frac{r_A r_B K_{AB}^2 \phi_{A_1} \phi_{B_1} U_A U_B}{\left(1 - r_A r_B K_{AB}^2 \phi_{A_1} \phi_{B_1} U_A U_B\right)^2} \tag{A10}$$

$$S_9 = \sum_i \sum_j n_{A_i B_j} + 2 \sum_i \sum_j \sum_k n_{A_i B_j A_k} + 3 \sum_i \sum_j \sum_k \sum_l n_{A_i B_j A_k B_l}$$

$$+ 4 \sum_i \sum_j \sum_k \sum_l \sum_m n_{A_i B_j A_k B_l A_m} + \dots$$

$$+ \sum_i \sum_j n_{B_i A_j} + 2 \sum_i \sum_j \sum_k n_{B_i A_j B_k} + 3 \sum_i \sum_j \sum_k \sum_l n_{B_i A_j B_k A_l}$$

$$+ 4 \sum_i \sum_j \sum_k \sum_l \sum_m n_{B_i A_j B_k A_l B_m} + \dots$$

$$= \left[\left(\frac{n_{B_1}}{r_A \phi_{B_1}} + \frac{n_{A_1}}{r_B \phi_{A_1}} \right) \frac{\left(1 + r_A r_B K_{AB}^2 \phi_{A_1} \phi_{B_1} U_A U_B\right)}{K_{AB}} \right.$$

$$\left. + 2\left(U_A n_{A_1} + U_B n_{B_1}\right) \right] \frac{r_A r_B K_{AB}^2 \phi_{A_1} \phi_{B_1} U_A U_B}{\left(1 - r_A r_B K_{AB}^2 \phi_{A_1} \phi_{B_1} U_A U_B\right)^2} \tag{A11}$$

$$S_{10} = \sum_i \sum_j n_{A_iB_jC} + 2\sum_i \sum_j \sum_k n_{A_iB_jA_kC} + 3\sum_i \sum_j \sum_k \sum_l n_{A_iB_jA_kB_lC}$$
$$+ 4\sum_i \sum_j \sum_k \sum_l \sum_m n_{A_iB_jA_kB_lA_mC} + \dots$$
$$+ \sum_i \sum_j n_{B_iA_jC} + 2\sum_i \sum_j \sum_k n_{B_iA_jB_kC} + 3\sum_i \sum_j \sum_k \sum_l n_{B_iA_jB_kA_lC}$$
$$+ 4\sum_i \sum_j \sum_k \sum_l \sum_m n_{B_iA_jB_kA_lB_mC} + \dots$$
$$= \frac{K'_{BC}\phi_{C_1}K'_{AB}}{r_C V} \sum_i n_{A_i} \sum_j n_{B_j} + \frac{2K'_{AC}\phi_{C_1}K'^2_{AB}}{r_C V^2} \sum_i n_{A_i} \sum_j n_{B_j} \sum_k n_{A_k}$$
$$+ \frac{3K'_{BC}\phi_{C_1}K'^3_{AB}}{r_C V^3} \sum_i n_{A_i} \sum_j n_{B_j} \sum_k n_{A_k} \sum_l n_{B_l}$$
$$+ \frac{4K'_{AC}\phi_{C_1}K'^4_{AB}}{r_C V^4} \sum_i n_{Ai} \sum_j n_{B_j} \sum_k n_{A_k} \sum_l n_{B_l} \sum_m n_{A_m} + \dots$$
$$+ \frac{K'_{AC}\phi_{C_1}K'_{AB}}{r_C V} \sum_i n_{B_i} \sum_j n_{A_j} + \frac{2K'_{BC}\phi_{C_1}K'^2_{AB}}{r_C V^2} \sum_i n_{B_i} \sum_j n_{A_j} \sum_k n_{B_k}$$
$$+ \frac{3K'_{AC}\phi_{C_1}K'^3_{AB}}{r_C V^3} \sum_i n_{B_i} \sum_j n_{A_j} \sum_k n_{B_k} \sum_l n_{A_l}$$
$$+ \frac{4K'_{BC}\phi_{C_1}K'^4_{AB}}{r_C V^4} \sum_i n_{B_i} \sum_j n_{A_j} \sum_k n_{B_k} \sum_l n_{A_l} \sum_m n_{B_m} + \dots$$
$$= \phi_{C_1}\left[\frac{r_B K_{BC} n_{B_1}}{r_A K_{AB} \phi_{B_1}} \left(r_A r_B K^2_{AB} \phi_{A_1} \phi_{B_1} U_A U_B \right) + 2 r_A K_{AC} U_A n_{A_1} \right.$$
$$\times \left(r_A r_B K^2_{AB} \phi_{A_1} \phi_{B_1} U_A U_B \right)$$
$$+ \frac{3 r_B K_{BC} n_{B_1}}{r_A K_{AB} \phi_{B_1}} \left(r_A r_B K^2_{AB} \phi_{A_1} \phi_{B_1} U_A U_B \right)^2 + 4 r_A K_{AC} U_A n_{A_1}$$
$$\times \left(r_A r_B K^2_{AB} \phi_{A_1} \phi_{B_1} U_A U_B \right)^2 + \dots$$
$$+ \frac{r_A K_{AC} n_{A_1}}{r_B K_{AB} \phi_{A_1}} \left(r_A r_B K^2_{AB} \phi_{A_1} \phi_{B_1} U_A U_B \right) + 2 r_B K_{BC} U_B n_{B_1}$$
$$\times \left(r_A r_B K^2_{AB} \phi_{A_1} \phi_{B_1} U_A U_B \right)$$
$$+ \frac{3 r_A K_{AC} n_{A_1}}{r_B K_{AB} \phi_{A_1}} \left(r_A r_B K^2_{AB} \phi_{A_1} \phi_{B_1} U_A U_B \right)^2 + 4 r_B K_{BC} U_B n_{B_1}$$
$$\left. \times \left(r_A r_B K^2_{AB} \phi_{A_1} \phi_{B_1} U_A U_B \right)^2 + \dots \right]$$

$$= \phi_{C_1}\left[\left(\frac{r_B K_{BC} n_{B_1}}{r_A K_{AB}\phi_{B_1}} + \frac{r_A K_{AC} n_{A_1}}{r_B K_{AB}\phi_{A_1}}\right)\sum_i (2i-1)\left(r_A r_B K_{AB}^2 \phi_{A_1}\phi_{B_1} U_A U_B\right)^i\right.$$

$$\left. + \left(r_A K_{AC} U_A n_{A_1} + r_B K_{BC} U_B n_{B_1}\right)\sum_i (2i)\left(r_A r_B K_{AB}^2 \phi_{A_1}\phi_{B_1} U_A U_B\right)^i\right]$$

$$= \phi_{C_1}\left[\left(\frac{r_B K_{BC} n_{B_1}}{r_A \phi_{B_1}} + \frac{r_A K_{AC} n_{A_1}}{r_B \phi_{A_1}}\right)\frac{\left(1 + r_A r_B K_{AB}^2 \phi_{A_1}\phi_{B_1} U_A U_B\right)}{K_{AB}}\right.$$

$$\left. + 2\left(r_A K_{AC} U_A n_{A_1} + r_B K_{BC} U_B n_{B_1}\right)\right]\frac{r_A r_B K_{AB}^2 \phi_{A_1}\phi_{B_1} U_A U_B}{\left(1 - r_A r_B K_{AB}^2 \phi_{A_1}\phi_{B_1} U_A U_B\right)^2} \quad \text{(A12)}$$

$$S_{11} = \sum_i n_{A_i C} = \frac{r_A K_{AC}\phi_{C_1} n_{A_1}}{\left(1 - K_A \phi_{A_1}\right)} = r_A K_{AC}\phi_{C_1} U_A n_{A_1} \quad \text{(A13)}$$

$$S_{12} = \sum_i\sum_j\sum_k n_{A_i B_j A_k C} + \sum_i\sum_j\sum_k\sum_l\sum_m n_{A_i B_j A_k B_l A_m C}$$

$$+ \sum_i\sum_j\sum_k\sum_l\sum_m\sum_n\sum_o n_{A_i B_j A_k B_l A_m B_n A_o C} + \ldots$$

$$+ \sum_i\sum_j n_{B_i A_j C} + \sum_i\sum_j\sum_k\sum_l n_{B_i A_j B_k A_l C}$$

$$+ \sum_i\sum_j\sum_k\sum_l\sum_m\sum_n n_{B_i A_j B_k A_l B_m A_n C} + \ldots$$

$$= \phi_{C_1}\left[r_A K_{AC} U_A n_{A_1}\left(r_A r_B K_{AB}^2 \phi_{A_1}\phi_{B_1} U_A U_B\right)\right.$$

$$+ r_A K_{AC} U_A n_{A_1}\left(r_A r_B K_{AB}^2 \phi_{A_1}\phi_{B_1} U_A U_B\right)^2 + \ldots$$

$$+ \frac{r_A K_{AC} n_{A_1}}{r_B K_{AB}\phi_{A_1}}\left(r_A r_B K_{AB}^2 \phi_{A_1}\phi_{B_1} U_A U_B\right)$$

$$\left. + \frac{r_A K_{AC} n_{A_1}}{r_B K_{AB}\phi_{A_1}}\left(r_A r_B K_{AB}^2 \phi_{A_1}\phi_{B_1} U_A U_B\right)^2 + \ldots\right]$$

$$= \phi_{C_1}\left(r_A K_{AC} U_A n_{A_1} + \frac{r_A K_{AC} n_{A_1}}{r_B K_{AB}\phi_{A_1}}\right)\sum_i \left(r_A r_B K_{AB}^2 \phi_{A_1}\phi_{B_1} U_A U_B\right)^i$$

$$= r_A K_{AC}\phi_{C_1}\left(U_A n_{A_1} + \frac{n_{A_1}}{r_B K_{AB}\phi_{A_1}}\right)\frac{r_A r_B K_{AB}^2 \phi_{A_1}\phi_{B_1} U_A U_B}{\left(1 - r_A r_B K_{AB}^2 \phi_{A_1}\phi_{B_1} U_A U_B\right)} \quad \text{(A14)}$$

$$S_{13} = \sum_i n_{B_i C} = \frac{r_B K_{BC}\phi_{C_1} n_{B_1}}{\left(1 - K_B \phi_{B_1}\right)} = r_B K_{BC}\phi_{C_1} U_B n_{B_1} \quad \text{(A15)}$$

$$S_{14} = \sum_i \sum_j \sum_k n_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{C}} + \sum_i \sum_j \sum_k \sum_l \sum_m n_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{A}_l\mathrm{B}_m\mathrm{C}}$$
$$+ \sum_i \sum_j \sum_k \sum_l \sum_m \sum_n \sum_o n_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{A}_l\mathrm{B}_m\mathrm{A}_n\mathrm{B}_o\mathrm{C}} + \cdots$$
$$+ \sum_i \sum_j n_{\mathrm{A}_i\mathrm{B}_j\mathrm{C}} + \sum_i \sum_j \sum_k \sum_l n_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{B}_l\mathrm{C}}$$
$$+ \sum_i \sum_j \sum_k \sum_l \sum_m \sum_n n_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{B}_l\mathrm{A}_m\mathrm{B}_n\mathrm{C}} + \cdots$$
$$= r_\mathrm{B} K_\mathrm{BC} \phi_{\mathrm{C}_1} \left(U_\mathrm{B} n_{\mathrm{B}_1} + \frac{n_{\mathrm{B}_1}}{r_\mathrm{A} K_\mathrm{AB} \phi_{\mathrm{B}_1}} \right) \frac{r_\mathrm{A} r_\mathrm{B} K_\mathrm{AB}^2 \phi_{\mathrm{A}_1} \phi_{\mathrm{B}_1} U_\mathrm{A} U_\mathrm{B}}{\left(1 - r_\mathrm{A} r_\mathrm{B} K_\mathrm{AB}^2 \phi_{\mathrm{A}_1} \phi_{\mathrm{B}_1} U_\mathrm{A} U_\mathrm{B}\right)} \qquad \text{(A16)}$$

The following relations hold for n_{A_1} and n_{B_1} [2].

$$n_{\mathrm{A}_1} = x_\mathrm{A} \phi_{\mathrm{A}_1} / \phi_\mathrm{A} \qquad \text{(A17)}$$

$$n_{\mathrm{B}_1} = x_\mathrm{B} \phi_{\mathrm{B}_1} / \phi_\mathrm{B} \qquad \text{(A18)}$$

Substitution of eqns. (A3–A18) into eqn. (A2) yields

$$H_\mathrm{f} = \frac{h_\mathrm{A} x_\mathrm{A} \bar{U}_\mathrm{A} \phi_{\mathrm{A}_1}}{\phi_\mathrm{A}} + \frac{h_\mathrm{B} x_\mathrm{B} \bar{U}_\mathrm{B} \phi_{\mathrm{B}_1}}{\phi_\mathrm{B}} + \left(h_\mathrm{A} \bar{U}_\mathrm{A} + h_\mathrm{AC} U_\mathrm{A}\right) \frac{r_\mathrm{A} K_\mathrm{AC} \phi_{\mathrm{C}_1} x_\mathrm{A} \phi_{\mathrm{A}_1}}{\phi_\mathrm{A}}$$
$$+ \left(h_\mathrm{B} \bar{U}_\mathrm{B} + h_\mathrm{BC} U_\mathrm{B}\right) \frac{r_\mathrm{B} K_\mathrm{BC} \phi_{\mathrm{C}_1} x_\mathrm{B} \phi_{\mathrm{B}_1}}{\phi_\mathrm{B}}$$
$$+ \left(h_\mathrm{A} \left\{ \frac{\bar{U}_\mathrm{A}}{K_\mathrm{AB} U_\mathrm{A}} \left(\frac{x_\mathrm{B}}{r_\mathrm{A} \phi_\mathrm{B}} + \frac{x_\mathrm{A}}{r_\mathrm{B} \phi_\mathrm{A}} \right) + \frac{\bar{U}_\mathrm{A} x_\mathrm{A} \phi_{\mathrm{A}_1}}{\phi_\mathrm{A}} \right.\right.$$
$$\times \left(2 - r_\mathrm{A} r_\mathrm{B} K_\mathrm{AB}^2 \phi_{\mathrm{A}_1} \phi_{\mathrm{B}_1} U_\mathrm{A} U_\mathrm{B}\right) + \frac{\bar{U}_\mathrm{A} U_\mathrm{B} x_\mathrm{B} \phi_{\mathrm{B}_1}}{U_\mathrm{A} \phi_\mathrm{B}}$$
$$+ \phi_{\mathrm{C}_1} \left[\left(\frac{r_\mathrm{B} K_\mathrm{BC} x_\mathrm{B}}{r_\mathrm{A} K_\mathrm{AB} \phi_\mathrm{B}} + \frac{r_\mathrm{A} K_\mathrm{AC} x_\mathrm{A}}{r_\mathrm{B} K_\mathrm{AB} \phi_\mathrm{A}} \right) \frac{\bar{U}_\mathrm{A}}{U_\mathrm{A}} + \frac{r_\mathrm{A} K_\mathrm{AC} \bar{U}_\mathrm{A} x_\mathrm{A} \phi_{\mathrm{A}_1}}{\phi_\mathrm{A}} \right.$$
$$\left.\left. \times \left(2 - r_\mathrm{A} r_\mathrm{B} K_\mathrm{AB}^2 \phi_{\mathrm{A}_1} \phi_{\mathrm{B}_1} U_\mathrm{A} U_\mathrm{B}\right) + \frac{r_\mathrm{B} K_\mathrm{BC} \bar{U}_\mathrm{A} U_\mathrm{B} x_\mathrm{B} \phi_{\mathrm{B}_1}}{U_\mathrm{A} \phi_\mathrm{B}} \right] \right\}$$
$$+ h_\mathrm{B} \left\{ \frac{\bar{U}_\mathrm{B}}{K_\mathrm{AB} U_\mathrm{B}} \left(\frac{x_\mathrm{B}}{r_\mathrm{A} \phi_\mathrm{B}} + \frac{x_\mathrm{A}}{r_\mathrm{B} \phi_\mathrm{A}} \right) + \frac{\bar{U}_\mathrm{B} x_\mathrm{B} \phi_{\mathrm{B}_1}}{\phi_\mathrm{B}} \right.$$
$$\times \left(2 - r_\mathrm{A} r_\mathrm{B} K_\mathrm{AB}^2 \phi_{\mathrm{A}_1} \phi_{\mathrm{B}_1} U_\mathrm{A} U_\mathrm{B}\right) + \frac{\bar{U}_\mathrm{B} U_\mathrm{A} x_\mathrm{A} \phi_{\mathrm{A}_1}}{U_\mathrm{B} \phi_\mathrm{A}}$$
$$+ \phi_{\mathrm{C}_1} \left[\left(\frac{r_\mathrm{B} K_\mathrm{BC} x_\mathrm{B}}{r_\mathrm{A} K_\mathrm{AB} \phi_\mathrm{B}} + \frac{r_\mathrm{A} K_\mathrm{AC} x_\mathrm{A}}{r_\mathrm{B} K_\mathrm{AB} \phi_\mathrm{A}} \right) \frac{\bar{U}_\mathrm{B}}{U_\mathrm{B}} + \frac{r_\mathrm{B} K_\mathrm{BC} \bar{U}_\mathrm{B} x_\mathrm{B} \phi_{\mathrm{B}_1}}{\phi_\mathrm{B}} \right.$$
$$\left.\left. \times \left(2 - r_\mathrm{A} r_\mathrm{B} K_\mathrm{AB}^2 \phi_{\mathrm{A}_1} \phi_{\mathrm{B}_1} U_\mathrm{A} U_\mathrm{B}\right) + \frac{r_\mathrm{A} K_\mathrm{AC} \bar{U}_\mathrm{B} U_\mathrm{A} x_\mathrm{A} \phi_{\mathrm{A}_1}}{U_\mathrm{B} \phi_\mathrm{A}} \right] \right\}$$

$$
+h_{AB}\left\{\left(\frac{x_B}{r_A\phi_B}+\frac{x_A}{r_B\phi_A}\right)\frac{\left(1+r_Ar_BK_{AB}^2\phi_{A_1}\phi_{B_1}U_AU_B\right)}{K_{AB}}\right.
$$

$$
+2\left(\frac{U_Ax_A\phi_{A_1}}{\phi_A}+\frac{U_Bx_B\phi_{B_1}}{\phi_B}\right)
$$

$$
+\phi_{C_1}\left[\left(\frac{r_BK_{BC}x_B}{r_A\phi_B}+\frac{r_AK_{AC}x_A}{r_B\phi_A}\right)\frac{\left(1+r_Ar_BK_{AB}^2\phi_{A_1}\phi_{B_1}U_AU_B\right)}{K_{AB}}\right.
$$

$$
\left.\left.+2\left(\frac{r_AK_{AC}U_Ax_A\phi_{A_1}}{\phi_A}+\frac{r_BK_{BC}U_Bx_B\phi_{B_1}}{\phi_B}\right)\right]\right\}
$$

$$
+\left[h_{AC}r_AK_{AC}\phi_{C_1}\left(\frac{U_Ax_A\phi_{A_1}}{\phi_A}+\frac{x_A}{r_AK_{AB}\phi_A}\right)+h_{BC}r_BK_{BC}\phi_{C_1}\right.
$$

$$
\left.\times\left(\frac{U_Bx_B\phi_{B_1}}{\phi_B}+\frac{x_B}{r_AK_{AB}\phi_B}\right)\right]
$$

$$
\left.\times\left(1-r_Ar_BK_{AB}^2\phi_{A_1}\phi_{B_1}U_AU_B\right)\right)\frac{r_Ar_BK_{AB}^2\phi_{A_1}\phi_{B_1}U_AU_B}{\left(1-r_Ar_BK_{AB}^2\phi_{A_1}\phi_{B_1}U_AU_B\right)^2} \qquad \text{(A19)}
$$

H_f reduces to H_{fA}^0 in pure alcohol A and to H_{fB}^0 in pure alcohol B, respectively.

$$
H_{fA}^0=\frac{h_AK_A\phi_{A_1}^{02}}{\left(1-K_A\phi_{A_1}^0\right)^2}=h_A\overline{U}_A^0\phi_{A_1}^0 \qquad \text{(A20)}
$$

$$
H_{fB}^0=\frac{h_BK_B\phi_{B_1}^{02}}{\left(1-K_B\phi_{B_1}^0\right)^2}=h_B\overline{U}_B^0\phi_{B_1}^0 \qquad \text{(A21)}
$$

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