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THERMODYNAMICS OF ALCOHOL SOLUTIONS: PHASE EQUILIBRIA OF BINARY AND TERNARY MIXTURES CONTAINING TWO ALCOHOLS

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ABSTRACT

The UNIQUAC associated-solution theory, proposed by Nagata for liquid mixtures containing any number of alcohols, is modified to give improved prediction of phase equilibria for ternary mixtures including two alcohols and one nonassociating component from only binary parameters. The proposed model assumes that chemical complex multimers are formed according to successive solvation reactions between pure *i*-mers of two alcohols. The calculated results show the reasonable quality of the proposed model.

INTRODUCTION

A number of chemical theories have been proposed to explain the thermodynamic properties of alcohol solutions by postulating that alcohols self-associate. Most of these theories have been developed for liquid solutions containing one alcohol and nonassociating components. Brandani and Evangelista [1] critically reconsidered the UNIQUAC associated-solution theory [2], clearly demonstrating the physical approximation of the model. Nagata [3] presented an extensive study on the phase equilibrium data reduction of binary and ternary alcohol solutions by means of the UNIQUAC associated-solution theory. The moderate deviations in predicted vapor-phase mole fractions for ternary mixtures containing two alcohols were obtained in comparison with those for ternary mixtures including one alcohol. This suggests that some improvements on the model will be necessary.

This paper presents an improved version of the UNIQUAC associated-solution theory for the accurate reproduction of the vapor pressure isotherms of binary alcohol–alcohol mixtures and for the good prediction of phase equilibria of ternary alcohols–nonassociating component mixtures from binary parameters alone.

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THEORY

Binary mixtures of two alcohols

We assume that the structural parameters, r_{A_i} and q_{A_i}, are given in terms of those for the monomer: $r_{A_i} = ir_A$ and $q_{A_i} = iq_A$, and that two alcohols, A and B, self-associate linearly and the association constants of consecutive reactions are defined by

$$K_A = \frac{C_{A_{i+1}}}{C_{A_i} C_{A_1} r_A} = \frac{\Phi_{A_{i+1}}}{\Phi_{A_i} \Phi_{A_1}} \frac{i}{(i+1)} \quad \text{for } A_i + A_1 = A_{i+1} \tag{1}$$

$$K_B = \frac{C_{B_{i+1}}}{C_{B_i} C_{B_1} r_B} = \frac{\Phi_{B_{i+1}}}{\Phi_{B_i} \Phi_{B_1}} \frac{i}{(i+1)} \quad \text{for } B_i + B_1 = B_{i+1} \tag{2}$$

We postulate successive solvation reactions forming complex alcohol multimers A_iB_j, $A_iB_jA_k$, $A_iB_jA_kB_l \ldots$ and that the solvation constant of various reactions is independent of the degree of association and solvation.

$$K_{AB} = \frac{C_{A_iB_j}}{C_{A_i} C_{B_j} r_A r_B} = \frac{\Phi_{A_iB_j}}{\Phi_{A_i} \Phi_{B_j}} \frac{r_{A_i} r_{B_j}}{r_{A_iB_j} r_A r_B} \quad \text{for } A_i + B_j = A_iB_j \tag{3}$$

$$K_{AB} = \frac{C_{A_iB_jA_k}}{C_{A_iB_j} C_{A_k} r_A r_B} = \frac{\Phi_{A_iB_jA_k}}{\Phi_{A_iB_j} \Phi_{A_k}} \frac{r_{A_iB_j} r_{A_k}}{r_{A_iB_jA_k} r_A r_B} \quad \text{for } A_iB_j + A_k = A_iB_jA_k \tag{4}$$

$$K_{AB} = \frac{C_{A_iB_jA_kB_l}}{C_{A_iB_jA_k} C_{B_l} r_A r_B} = \frac{\Phi_{A_iB_jA_kB_l}}{\Phi_{A_iB_jA_k} \Phi_{B_l}} \frac{r_{A_iB_jA_k} r_{B_l}}{r_{A_iB_jA_kB_l} r_A r_B} \quad \text{for } A_iB_jA_k + B_l = A_iB_jA_kB_l \tag{5}$$

Additionally, B_iA_j, $B_iA_jB_k$, $B_iA_jB_kA_l, \ldots$ are also formed. It is again assumed that $r_{A_iB_j} = ir_A + jr_B$ and $q_{A_iB_j} = iq_A + jq_B$ and so on. In the previous approach [3], only eqn. (3) was considered and this assumption may not agree with real molecular behaviors of mixtures including two associating components.

The activity coefficients of the components A and B are expressed by

$$\begin{aligned} \ln \gamma_A = {} & \ln\left(\Phi_{A_1}/\Phi^0_{A_1} x_A\right) + r_A\left(1/V^0_A - 1/V\right) \\ & - (Z/2) q_A \left[\ln(\Phi_A/\theta_A) + 1 - \Phi_A/\theta_A\right] \\ & + q_A\left[-\ln(\theta_A + \theta_B \tau_{BA}) + \theta_B\{\tau_{BA}/(\theta_A + \theta_B \tau_{BA}) - \tau_{AB}/(\theta_B + \theta_A \tau_{AB})\}\right] \end{aligned} \tag{6}$$

$$\begin{aligned} \ln \gamma_B = {} & \ln\left(\Phi_{B_1}/\Phi^0_{B_1} x_B\right) + r_B\left(1/V^0_B - 1/V\right) \\ & - (Z/2) q_B \left[\ln(\Phi_B/\theta_B) + 1 - \Phi_B/\theta_B\right] \\ & + q_B\left[-\ln(\theta_B + \theta_A \tau_{AB}) + \theta_A\{\tau_{AB}/(\theta_B + \theta_A \tau_{AB}) - \tau_{BA}/(\theta_A + \theta_B \tau_{BA})\}\right] \end{aligned} \tag{7}$$

where Φ_{A_1} and Φ_{B_1} are the monomer segment fractions of both components, the segment fraction Φ, the surface fraction θ and the coefficient τ are defined as follows.

$$\Phi_A = r_A x_A/(r_A x_A + r_B x_B)$$

$$\Phi_B = 1 - \Phi_A \tag{8}$$

$$\theta_A = q_A x_A/(q_A x_A + q_B x_B)$$

$$\theta_B = 1 - \theta_A \tag{9}$$

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

$$\tau_{AB} = \exp(-a_{AB}/T) \tag{10}$$

The energy parameters, a_{BA} and a_{AB}, are obtained from experimental phase equilibrium data.

The nominal segment fractions of the two components are related to the monomeric segment fractions and the equilibrium constants (see Appendix A).

$$\Phi_A = \bar{S}_A + \frac{r_A}{\left(1 - r_A r_B K_{AB}^2 S_A S_B\right)^2} \times \left[2K_{AB}\bar{S}_A S_B + r_B K_{AB}^2 \bar{S}_A S_A S_B\left(2 - r_A r_B K_{AB}^2 S_A S_B\right) + r_A K_{AB}^2 \bar{S}_A S_B^2\right] \tag{11}$$

$$\Phi_B = \bar{S}_B + \frac{r_B}{\left(1 - r_A r_B K_{AB}^2 S_A S_B\right)^2} \times \left[2K_{AB} S_A \bar{S}_B + r_A K_{AB}^2 S_A \bar{S}_B S_B\left(2 - r_A r_B K_{AB}^2 S_A S_B\right) + r_B K_{AB}^2 S_A^2 \bar{S}_B\right] \tag{12}$$

where the sums $\bar{S}_A$, $\bar{S}_B$, S_A and S_B are defined as follows

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

$$\bar{S}_B = \sum_{i=1}^{\infty} \Phi_{B_1} = \Phi_{B_i}/\left(1 - K_B \Phi_{B_1}\right)^2 \tag{14}$$

$$S_A = \sum_{i=1}^{\infty} \Phi_{A_i}/i = \Phi_{A_1}/\left(1 - K_A \Phi_{A_1}\right) \tag{15}$$

$$S_B = \sum_{i=1}^{\infty} \Phi_{B_i}/i = \Phi_{B_1}/\left(1 - K_B \Phi_{B_1}\right) \tag{16}$$

As shown in Appendix B, the true molar volume of the mixture is given by

$$\frac{1}{V} = \frac{S_A}{r_A} + \left(\frac{2}{r_A r_B K_{AB}} + \frac{S_A}{r_A} + \frac{S_B}{r_B}\right) \frac{r_A r_B K_{AB}^2 S_A S_B}{\left(1 - r_A r_B K_{AB}^2 S_A S_B\right)} + \frac{S_B}{r_B} \tag{17}$$

$\Phi_{A_1}^0$ and $1/V_A^0$ of pure alcohol A are expressed as

$$\Phi_{A_1}^0 = \left[2K_A + 1 - (1 + 4K_A)^{1/2}\right]/2K_A^2 \tag{18}$$

$$1/V_A^0 = \left(1 - K_A \Phi_{A_1}^0\right)/r_A \tag{19}$$

The corresponding expressions for pure alcohol B are derived by changing the subscript A to B.

Binary mixtures including one alcohol and one nonassociating component

In this case the component B is a nonassociating component. We assume that the alcohol *i*-mers form chemical complexes A_iB with the component B by solvation and the solvation constant is defined by

$$K_{AB} = \frac{C_{A_iB}}{C_{A_i} C_{B_1} r_A r_B} = \frac{\Phi_{A_iB}}{\Phi_{A_i}\Phi_{B_1}} \frac{r_{A_i}}{r_{A_iB} r_A} \quad \text{for } A_i + B_1 = A_iB \tag{20}$$

The activity coefficient of the component B is given by putting $\Phi^0_{B_1} = 1$ in eqn. (7).

The monomer segment fractions are obtained by solving the following mass balance equations.

$$\Phi_A = \left[\Phi_{A_1}/(1 - K_A\Phi_{A_1})^2\right]\left[1 + r_A K_{AB}\Phi_{B_1}\right] \tag{21}$$

$$\Phi_B = \Phi_{B_1}\left[1 + r_B K_{AB}\Phi_{A_1}/(1 - K_A\Phi_{A_1})\right] \tag{22}$$

The true molar volume of the mixture is expressed by

$$1/V = \Phi_{A_1}/r_A(1 - K_A\Phi_{A_1}) + (\Phi_{B_1}/r_B)\left[1 + r_B K_{AB}\Phi_{A_1}/(1 - K_A\Phi_{A_1})\right] \tag{23}$$

Ternary mixtures including two alcohols and one nonassociating component

Symbols A, B and C stand for two alcohols and nonassociating component. In addition to the preceding reactions to form alcohol *i*-mers and complex alcohol multimers, we should consider that ternary solvation reactions are of the form

$$\begin{array}{ll}
A_iB_j + C_1 = A_iB_jC & B_iA_j + C_1 = B_iA_jC \\
A_iB_jA_k + C_1 = A_iB_jA_kC & B_iA_jB_k + C_1 = B_iA_jB_kC \\
\vdots & \vdots \\
(A_iB_j)_m + C_1 = (A_iB_j)_mC & (B_iA_j)_m + C_1 = (B_iA_j)_mC \\
A_i(B_jA_k)_m + C_1 = A_i(B_jA_k)_mC & B_i(A_jB_k)_m + C_1 = B_i(A_jB_k)_mC
\end{array}$$

where the indices i, j, k and m go from unity to infinity. Further, we assume that the solvation constant of $(A_iB_j)_mC$-forming reaction is K_{BC} and that for $(B_iA_j)_mC$ is K_{AC}. Thus, any ternary equilibrium constants are unnecessary in pertinent equations described below.

The activity coefficient of any component I in the ternary mixture is

$$\ln \gamma_I = \ln\left(\Phi_{I_1}/\Phi^0_{I_1}x_I\right) + r_I\left(1/V_I^0 - 1/V\right) - (Z/2)q_I\left[\ln(\Phi_I/\theta_I) + 1 - \Phi_I/\theta_I\right] + q_I\left[1 - \ln\left(\sum_J \theta_I\tau_{JI}\right) - \sum_J\left(\theta_J\tau_{IJ}/\sum_K \theta_K\tau_{KJ}\right)\right] \tag{24}$$

where for component C, $\Phi^0_{\mathrm{C}_1} = 1$ and

$$\Phi_{\mathrm{I}} = r_{\mathrm{I}} x_{\mathrm{I}} / \sum_J r_{\mathrm{J}} x_{\mathrm{J}} \tag{25}$$

$$\theta_{\mathrm{I}} = q_{\mathrm{I}} x_{\mathrm{I}} / \sum_J q_{\mathrm{J}} x_{\mathrm{J}} \tag{26}$$

$$1/V^0_{\mathrm{I}} = \left(1 - K_{\mathrm{I}} \Phi^0_{\mathrm{I}_1}\right)/r_{\mathrm{I}} \tag{27}$$

$$\tau_{\mathrm{JI}} = \exp(-a_{\mathrm{JI}}/T) \tag{28}$$

The monomer segment fractions Φ_{I_1} are obtained from a simultaneous solution of the following mass balance equations (see Appendix A).

$$\begin{aligned}\Phi_{\mathrm{A}} = {} & \left(1 + r_{\mathrm{A}} K_{\mathrm{AC}} \Phi_{\mathrm{C}_1}\right) \bar{S}_{\mathrm{A}} + \frac{r_{\mathrm{A}}}{\left(1 - r_{\mathrm{A}} r_{\mathrm{B}} K^2_{\mathrm{AB}} S_{\mathrm{A}} S_{\mathrm{B}}\right)^2} \\ & \times \big[2 K_{\mathrm{AB}} \bar{S}_{\mathrm{A}} S_{\mathrm{B}} + r_{\mathrm{B}} K^2_{\mathrm{AB}} \bar{S}_{\mathrm{A}} S_{\mathrm{A}} S_{\mathrm{B}} \left(2 - r_{\mathrm{A}} r_{\mathrm{B}} K^2_{\mathrm{AB}} S_{\mathrm{A}} S_{\mathrm{B}}\right) + r_{\mathrm{A}} K^2_{\mathrm{AB}} \bar{S}_{\mathrm{A}} S^2_{\mathrm{B}} \\ & + \Phi_{\mathrm{C}_1} (\{ r_{\mathrm{A}} K_{\mathrm{AC}} + r_{\mathrm{B}} K_{\mathrm{BC}}) K_{\mathrm{AB}} \bar{S}_{\mathrm{A}} S_{\mathrm{B}} + r_{\mathrm{A}} r_{\mathrm{B}} K^2_{\mathrm{AB}} K_{\mathrm{AC}} \bar{S}_{\mathrm{A}} S_{\mathrm{A}} S_{\mathrm{B}} \\ & \times \left(2 - r_{\mathrm{A}} r_{\mathrm{B}} K^2_{\mathrm{AB}} S_{\mathrm{A}} S_{\mathrm{B}}\right) + r_{\mathrm{A}} r_{\mathrm{B}} K^2_{\mathrm{AB}} K_{\mathrm{BC}} \bar{S}_{\mathrm{A}} S^2_{\mathrm{B}} \} \big]\end{aligned} \tag{29}$$

$$\begin{aligned}\Phi_{\mathrm{B}} = {} & \left(1 + r_{\mathrm{B}} K_{\mathrm{BC}} \Phi_{\mathrm{C}_1}\right) \bar{S}_{\mathrm{B}} + \frac{r_{\mathrm{B}}}{\left(1 - r_{\mathrm{A}} r_{\mathrm{B}} K^2_{\mathrm{AB}} S_{\mathrm{A}} S_{\mathrm{B}}\right)^2} \\ & \times \big[2 K_{\mathrm{AB}} S_{\mathrm{A}} \bar{S}_{\mathrm{B}} + r_{\mathrm{A}} K^2_{\mathrm{AB}} S_{\mathrm{A}} \bar{S}_{\mathrm{B}} S_{\mathrm{B}} \left(2 - r_{\mathrm{A}} r_{\mathrm{B}} K^2_{\mathrm{AB}} S_{\mathrm{A}} S_{\mathrm{B}}\right) + r_{\mathrm{B}} K^2_{\mathrm{AB}} S^2_{\mathrm{A}} \bar{S}_{\mathrm{B}} \\ & + \Phi_{\mathrm{C}_1} \{ (r_{\mathrm{A}} K_{\mathrm{AC}} + r_{\mathrm{B}} K_{\mathrm{BC}}) K_{\mathrm{AB}} S_{\mathrm{A}} \bar{S}_{\mathrm{B}} + r_{\mathrm{A}} r_{\mathrm{B}} K^2_{\mathrm{AB}} K_{\mathrm{BC}} S_{\mathrm{A}} \bar{S}_{\mathrm{B}} S_{\mathrm{B}} \\ & \times \left(2 - r_{\mathrm{A}} r_{\mathrm{B}} K^2_{\mathrm{AB}} S_{\mathrm{A}} S_{\mathrm{B}}\right) + r_{\mathrm{A}} r_{\mathrm{B}} K^2_{\mathrm{AB}} K_{\mathrm{AC}} S^2_{\mathrm{A}} \bar{S}_{\mathrm{B}} \} \big]\end{aligned} \tag{30}$$

$$\begin{aligned}\Phi_{\mathrm{C}} = \Phi_{\mathrm{C}_1} & \Bigg[1 + r_{\mathrm{C}} K_{\mathrm{AC}} S_{\mathrm{A}} + r_{\mathrm{C}} K_{\mathrm{BC}} S_{\mathrm{B}} + \frac{r_{\mathrm{A}} r_{\mathrm{B}} r_{\mathrm{C}} K^2_{\mathrm{AB}} S_{\mathrm{A}} S_{\mathrm{B}}}{\left(1 - r_{\mathrm{A}} r_{\mathrm{B}} K^2_{\mathrm{AB}} S_{\mathrm{A}} S_{\mathrm{B}}\right)} \\ & \times \left(\frac{K_{\mathrm{AC}}}{r_{\mathrm{B}} K_{\mathrm{AB}}} + \frac{K_{\mathrm{BC}}}{r_{\mathrm{A}} K_{\mathrm{AB}}} + K_{\mathrm{AC}} S_{\mathrm{A}} + K_{\mathrm{BC}} S_{\mathrm{B}} \right) \Bigg]\end{aligned} \tag{31}$$

The true molar volume is expressed as follows (see Appendix B).

$$\begin{aligned}\frac{1}{V} = {} & \frac{S_{\mathrm{A}}}{r_{\mathrm{A}}} + \frac{S_{\mathrm{B}}}{r_{\mathrm{B}}} + \left(\frac{2}{r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}}} + \frac{S_{\mathrm{A}}}{r_{\mathrm{A}}} + \frac{S_{\mathrm{B}}}{r_{\mathrm{B}}} \right) \frac{r_{\mathrm{A}} r_{\mathrm{B}} K^2_{\mathrm{AB}} S_{\mathrm{A}} S_{\mathrm{B}}}{\left(1 - r_{\mathrm{A}} r_{\mathrm{B}} K^2_{\mathrm{AB}} S_{\mathrm{A}} S_{\mathrm{B}}\right)} \\ & + \frac{\Phi_{\mathrm{C}_1}}{r_{\mathrm{C}}} \Bigg[1 + r_{\mathrm{C}} K_{\mathrm{AC}} S_{\mathrm{A}} + r_{\mathrm{C}} K_{\mathrm{BC}} S_{\mathrm{B}} + \Bigg\{ \left(\frac{1}{r_{\mathrm{B}} K_{\mathrm{AB}}} + S_{\mathrm{A}} \right) K_{\mathrm{AC}} \\ & + \left(\frac{1}{r_{\mathrm{A}} K_{\mathrm{AB}}} + S_{\mathrm{B}} \right) K_{\mathrm{BC}} \Bigg\} \frac{r_{\mathrm{A}} r_{\mathrm{B}} r_{\mathrm{C}} K^2_{\mathrm{AB}} S_{\mathrm{A}} S_{\mathrm{B}}}{\left(1 - r_{\mathrm{A}} r_{\mathrm{B}} K^2_{\mathrm{AB}} S_{\mathrm{A}} S_{\mathrm{B}}\right)} \Bigg]\end{aligned} \tag{32}$$

The association constants of pure alcohols at 50°C are as follows: 173.9 for methanol; 110.4 for ethanol; 49.1 for 2-propanol. Brandani [4] estimated these equilibrium constants for the association of pure compounds from the properties of pure substances. The enthalpy of hydrogen bond formation was assumed to be -23.2 kJ mol^{-1} [5] for all alcohols studied here and to be independent of temperature and of the degree of association. This value fixes the temperature dependence of the association constant according to the van't Hoff equation. The pure-component structural parameters, r and q, were calculated from the method of Vera et al. [6].

The thermodynamic equation used to reduce experimental vapor–liquid equilibrium data is

$$\phi_I y_I P = \gamma_I x_I \phi_I^s P_I^s \exp\left[v_I^L (P - P_I^s)/RT \right] \tag{33}$$

where y, P and P^s are the vapor-phase mole fraction, total pressure and pure component vapor pressure, respectively. P^s is calculated from the Antoine equation whose constants are available in the literature [7,8]. The molar pure liquid volume v^L is estimated using the modified Rackett equation [9].

The fugacity coefficients, ϕ_I at P and ϕ_I^s at P^s, are obtained from the relation

$$\ln \phi_I = \left(2 \sum_J i y_I B_{IJ} - \sum_I \sum_J y_I y_J B_{IJ} \right) \frac{P}{RT} \tag{34}$$

where the second virial coefficients B_{IJ} are calculated by use of the generalized method of Hayden and O'Connell [10].

The computer program used is similar to that described by Prausnitz et al. [11], based on the maximum likelihood principle. An optimum set of the energy parameters was derived by minimizing the objective function defined by

$$F = \sum_{i=1}^{N} \left[\frac{(P_i - \hat{P}_i)^2}{\sigma_P^2} + \frac{(T_i - \hat{T}_i)^2}{\sigma_T^2} + \frac{(x_{A_i} - \hat{x}_{A_i})^2}{\sigma_x^2} + \frac{(y_{A_i} - \hat{y}_{A_i})^2}{\sigma_y^2} \right] \tag{35}$$

where a circumflex denotes the calculated true value corresponding to each experimental point and the standard deviations in the measured values were set as: $\sigma_P = 1.0$ Torr for pressure; $\sigma_T = 0.05$ K for temperature; $\sigma_x = 0.001$ for liquid-phase mole fraction; $\sigma_y = 0.003$ for vapor-phase mole fraction.

A set of the energy parameters for a partially miscible mixture is obtained by solving eqn. (36) by means of the Newton–Raphson method.

$$(\gamma_I x_I)^I = (\gamma_I x_I)^{II} \tag{36}$$

where the subscripts, I and II, represent two liquid phases in equilibrium.

TABLE 1

Solvation equilibrium constants and enthalpies of complex formation

Mixture (A–B)	K_{AB} (50°C)	$-h_{AB}$ (kJ mol^{-1})
Methanol–benzene	4	8.3
Methanol–chlorobenzene	2 (55°C)	
Methanol–ethanol	130	23.2
Methanol–2-propanol	70	23.2
Ethanol–benzene	3	8.3
2-Propanol–chlorobenzene	1 (55°C)	

CALCULATED RESULTS

Binary mixtures

Table 1 gives the solvation equilibrium constants and enthalpies of complex formation [3]. The solvation constants for alcohol–alcohol mixtures obtained in this work are not so large as the old values reported previously [3]. Table 2 shows the results of binary phase equilibrium data reduction. Figure 1 compares the calculated results with the experimental vapor–liquid equilibria of two alcohol–alcohol mixtures with good accuracy. In these calculations K_{AB} is an adjustable parameter and the energy parameters were taken as non-zero values.

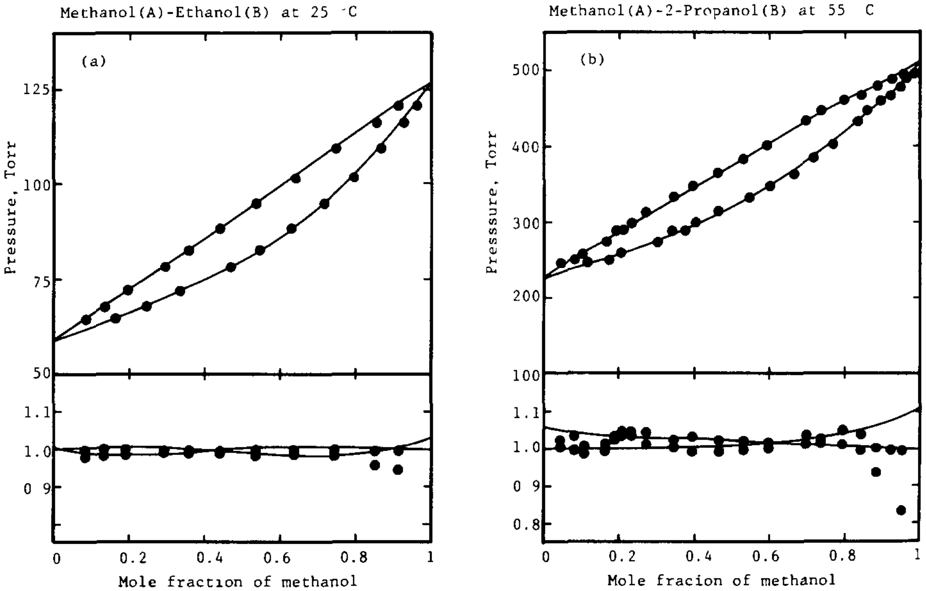

Fig. 1. Vapor–liquid equilibria for binary alcohol–alcohol mixtures. Experimental (●), calculated (———). (a) Methanol–ethanol at 25°C [12]; (b) methanol–2-propanol at 55°C [13].

TABLE 2

Binary calculated results obtained from phase equilibrium data reduction

Mixture (A–B)	Temp. (°C)	No. of data points	Root-mean square deviations				Parameters (K)		Ref.
			δP (Torr)	δT (°C)	δx ($\times 10^3$)	δy ($\times 10^3$)	a_{AB}	a_{BA}	
Methanol–ethanol	25	12	0.51	0.00	0.2	1.5	−17.19	150.68	12
Methanol–2-propanol	55	20	1.78	0.07	0.9	3.8	−87.96	208.01	13
Methanol–benzene	25	26	3.05	0.00	1.2		−122.62	294.54	12
Methanol–chlorobenzene	55	13	1.51	0.06	1.6	3.3	−45.75	139.71	14
Ethanol–benzene	25	11	0.76	0.00	1.0	5.5	−35.50	141.02	15
Ethanol–cyclohexane	20	7	0.77	0.01	0.3	3.3	103.02	−29.63	13
Ethanol–methylcyclohexane	35	8	0.24	0.00	0.3	1.8	60.58	−9.61	13
2-Propanol–chlorobenzene	55	12	1.22	0.00	0.5	3.4	117.25	−35.22	16
2-Propanol–cyclohexane	50	9	1.10	0.04	0.4	3.8	155.98	−84.76	17
2-Propanol–*n*-hexane	55.06	24	1.08	0.00	0.4	1.4	175.93	−97.83	12
Methanol–cyclohexane	25	MS [a]					7.86	86.15	18
Methanol–*n*-hexane	5	MS					48.03	45.73	19
	25	MS					9.71	74.99	19
Methanol–methylcyclohexane	25	MS					15.24	63.05	20

[a] MS = mutal solubilities.

TABLE 3

Ternary predicted results of vapor–liquid equilibria obtained from binary parameters

Mixture	Temp. (°C)	No. of data points	Absolute arithmetic mean deviations						Reference
			δy ($\times 10^3$)		δP (Torr)		$\delta P/P$ (%)		
			I [a]	II [b]	I	II	I	II	
Methanol–			6.0	11.9					
ethanol–	25	24	6.7	8.3	3.2	2.2	2.3	1.6	21
benzene			9.5	16.5					
Methanol–			6.1	12.7					
2-propanol–	55	15	5.2	9.4	4.4	5.1	1.4	1.6	16
chlorobenzene			4.4	3.9					

[a] I, This work.
[b] II, Nagata [3].

Ternary mixtures

Ternary predictions of vapor–liquid and liquid–liquid equilibria for mixtures containing two alcohols and one nonassociating component have been made with only the binary parameters listed in Table 2. Table 3 presents the results of vapor–liquid equilibrium prediction for two mixtures, clearly indicating that the proposed model decreases the deviations in vapor-phase mole fractions with good success. Table 4 gives a detailed comparison of the calculated results with the experimental data of methanol–ethanol–benzene

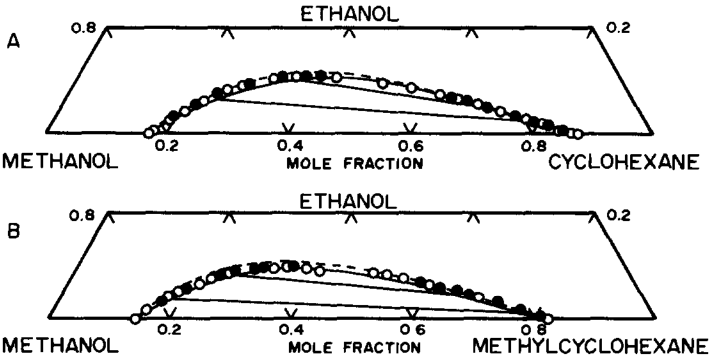

Fig. 2. Ternary liquid–liquid equilibria for mixtures containing two alcohols and one saturated hydrocarbon. Experimental: tie line (●); solubility (○). Calculated (———) this work; (- - - - -) previous work [3]. A, Methanol–ethanol–cyclohexane at 25°C [22]; B, methanol–ethanol–methylcyclohexane at 25°C [20]; C, methanol–2-propanol–*n*-hexane at 5°C [19]; D, methanol–2-propanol–*n*-hexane at 25°C [19]; E, methanol–2-propanol–cyclohexane at 25°C [23].

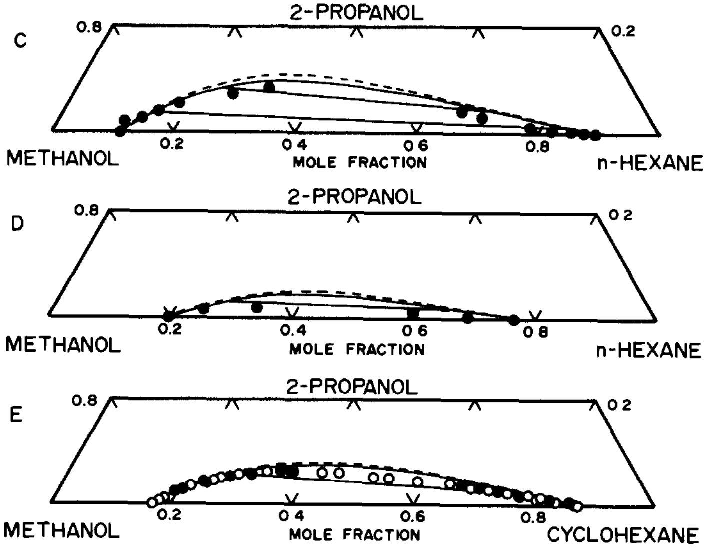

Fig. 2 (continued).

at 25°C. Figure 2 shows observed and calculated liquid–liquid equilibria for five mixtures. Pando et al. [24] presented an association model for the excess Gibbs energy of binary alcohol—alcohol solutions and did not extend the model to ternary alcohol mixtures.

In conclusion, the binary and ternary calculated results confirm the reliable quality of the proposed model and our approach for alcohol–alcohol mixtures is more reasonable than the previous one [3].

LIST OF SYMBOLS

A, B, C	alcohols and nonassociating component
C	molar concentration
a_{IJ}	binary interaction parameter
F	objective function of eqn. (35)
h_{AB}	enthalpy of complex formation
K_A, K_B	association constants
K_{AB}, K_{AC}, K_{BC}	equilibrium constants of complex formation
P	total pressure
P_I^s	saturated vapor pressure of pure component I
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. (13) and (14)
S_A, S_B	sums as defined by eqns. (15) and (16)
T	absolute temperature

TABLE 4

Comparsion of calculated and experimental vapor–liquid equilibrium data for methanol(A)–ethanol(B)–benzene(C) at 25°C

No.	Experimental							Deviations [a]			
	x_A	x_B	x_C	y_A	y_B	y_C	P(Torr)	$\Delta y_A(\times 10^3)$	$\Delta y_B(\times 10^3)$	$\Delta y_C(\times 10^3)$	ΔP(Torr)
1	0.089	0.229	0.682	0.176	0.202	0.622	141.9	0.8	2.2	−3.0	2.77
2	0.269	0.065	0.666	0.439	0.045	0.516	169.0	−10.8	7.5	3.5	−2.67
3	0.464	0.073	0.463	0.487	0.040	0.473	179.3	1.7	11.6	−13.3	3.88
4	0.682	0.089	0.229	0.569	0.032	0.399	171.6	12.6	1.6	−14.2	2.36
5	0.544	0.136	0.320	0.499	0.059	0.442	168.1	9.5	9.7	−19.3	−0.19
6	0.326	0.143	0.531	0.398	0.085	0.517	165.8	−14.6	16.2	−1.7	1.15
7	0.106	0.131	0.763	0.267	0.137	0.596	149.6	−1.5	4.6	−3.2	1.72
8	0.132	0.351	0.517	0.189	0.221	0.590	145.7	8.5	2.8	−11.3	7.40
9	0.267	0.269	0.464	0.319	0.151	0.530	157.6	−1.7	15.5	−13.8	6.45
10	0.303	0.337	0.360	0.329	0.159	0.512	147.8	6.4	3.2	−9.6	0.74
11	0.359	0.333	0.308	0.365	0.148	0.487	155.6	4.0	2.8	−6.8	7.80
12	0.533	0.365	0.102	0.527	0.163	0.310	135.5	−8.3	−4.0	12.3	7.10
13	0.648	0.291	0.061	0.645	0.131	0.224	131.0	−13.0	−4.5	17.5	5.63
14	0.460	0.475	0.065	0.516	0.247	0.237	115.3	−3.8	−4.9	8.6	3.40
15	0.335	0.573	0.092	0.382	0.299	0.319	113.5	−2.8	−13.9	16.6	3.53
16	0.283	0.487	0.230	0.297	0.237	0.466	134.7	4.4	4.8	−9.1	2.96
17	0.141	0.555	0.304	0.165	0.288	0.547	127.8	8.9	−3.0	−6.0	0.10
18	0.077	0.475	0.448	0.101	0.289	0.610	128.1	3.9	3.3	−7.2	−2.12
19	0.073	0.699	0.228	0.089	0.385	0.526	114.6	5.5	−1.0	−4.4	−0.64
20	0.245	0.695	0.060	0.323	0.422	0.255	100.1	2.5	−19.0	16.5	5.34
21	0.063	0.874	0.063	0.096	0.619	0.285	85.6	2.5	−10.5	8.0	2.08
22	0.404	0.216	0.380	0.416	0.096	0.488	161.8	3.6	6.3	−9.9	2.01
23	0.189	0.466	0.345	0.219	0.235	0.546	138.5	9.8	−3.3	−6.5	3.63
24	0.191	0.234	0.575	0.286	0.149	0.565	150.1	2.8	4.2	−7.0	1.16
Root-mean square deviation								7.2	8.4	10.7	3.9

[a] Deviation = experimental value − calculated one.

V	true molar volume of the mixture
v_{I}^{0}	true molar volume of pure alcohol I
$v_{\mathrm{I}}^{\mathrm{L}}$	molar liquid volume of pure component I
x_{I}	liquid-phase mole fraction of component I
y_{I}	vapor-phase mole fraction of component I
Z	lattice coordination number equal to 10

Greek letters

γ_{I}	activity coefficient of component I
θ_{I}	surface fraction of component I
σ_P, σ_T, σ_x, σ_y	standard deviations in pressure, temperature, liquid-phase mole fraction and vapor-phase mole fraction, respectively
τ_{IJ}	coefficient as defined by $\exp(-a_{\mathrm{IJ}}/T)$
Φ_{I}	segment fraction of component I
Φ_{I_1}	monomer segment fraction of component I
ϕ_{I}	vapor phase fugacity coefficient of component I
$\phi_{\mathrm{I}}^{\mathrm{s}}$	vapor-phase fugacity coefficient of pure component I at T and $P_{\mathrm{I}}^{\mathrm{s}}$

Subscripts

A, B, C	alcohols and nonassociating component
A_1, B_1, C_1	monomers of components A, B and C
A_i, B_i	i-mers of alcohols
$\mathrm{A}_i\mathrm{B}_j\mathrm{C}$	complex containing i molecules of alcohol A and j molecules of alcohol B and one molecule of component C
$\mathrm{A}_i\mathrm{C}$	complex containing i molecules of alcohol A and one molecule of component C
$\mathrm{B}_i\mathrm{C}$	complex containing i molecules of alcohol B and one molecule of component C
AB, AC, BC	binary complexes
I, J, K	components I, J and K
i, j, k, l, m	i, j, k, l and m-mers of alcohols or indices

Superscripts

^{0}	pure alcohol reference state
$\hat{}$	calculated property

APPENDIX A

DERIVATION OF THE EXPRESSIONS FOR THE MASS BALANCE EQUATIONS

Binary alcohol(A)–alcohol(B)-mixtures

Note that we distinguish $\mathrm{A}_i\mathrm{B}_j$ from $\mathrm{B}_i\mathrm{A}_j$, because the right hand molecule of $\mathrm{A}_i\mathrm{B}_j$, B, has a free hydroxyl group, on the other hand, the right hand molecule of B_iA_j is A, which keeps a free hydroxyl group, and this relation holds for other complex multimers. A total mass balance yields

$$\begin{aligned}\Phi_A = {} & \sum_i \Phi_{A_i} + \sum_i \sum_j \Phi_{A_iB_j} \frac{r_{A_i}}{r_{A_iB_j}} + \sum_i \sum_j \sum_k \Phi_{A_iB_jA_k} \frac{r_{A_iA_k}}{r_{A_iB_jA_k}} \\ & + \sum_i \sum_j \sum_k \sum_l \Phi_{A_iB_jA_kB_l} \frac{r_{A_iA_k}}{r_{A_iB_jA_kB_l}} + \ldots + \sum_i \sum_j \Phi_{B_iA_j} \frac{r_{A_j}}{r_{B_iA_j}} \\ & + \sum_i \sum_j \sum_k \Phi_{B_iA_jB_k} \frac{r_{A_j}}{r_{B_iA_jB_k}} + \sum_i \sum_j \sum_k \sum_l \Phi_{B_iA_jB_kA_l} \frac{r_{A_jA_l}}{r_{B_iA_jB_kA_l}} + \ldots \qquad \text{(A1)}\end{aligned}$$

where Σ_i denotes $\Sigma_{i=1}^{\infty}$. According to the definition of the solvation constant, $\Phi_{A_iB_j}$, $\Phi_{A_iB_jA_k}$ and $\Phi_{A_iB_jA_kB_l}$ etc., are expressed as follows

$$\Phi_{A_iB_j} = K'_{AB} \Phi_{A_i} \Phi_{B_j} \frac{r_{A_iB_j}}{r_{A_i} r_{B_j}} \qquad \text{(A2)}$$

$$\Phi_{A_iB_jA_k} = K'^2_{AB} \Phi_{A_i} \Phi_{B_j} \Phi_{A_k} \frac{r_{A_iB_jA_k}}{r_{A_i} r_{B_j} r_{A_k}} \qquad \text{(A3)}$$

$$\Phi_{A_iB_jA_kB_l} = K'^3_{AB} \Phi_{A_i} \Phi_{B_j} \Phi_{A_k} \Phi_{B_l} \frac{r_{A_iB_jA_kB_l}}{r_{A_i} r_{B_j} r_{A_k} r_{B_l}} \qquad \text{(A4)}$$

where $K'_{AB} = r_A r_B K_{AB}$.

Inserting eqns. (A2–A4) into eqn. (A1) and recalling $r_{A_iA_k} = r_{A_i} + r_{A_k}$ yields

$$\begin{aligned}\Phi_A = {} & \sum_i \Phi_{A_i} + K'_{AB} \sum_i \Phi_{A_i} \sum_j \frac{\Phi_{B_j}}{r_{B_j}} + K'^2_{AB} \sum_i \sum_j \sum_k \Phi_{A_i} \Phi_{B_j} \Phi_{A_k} \frac{(r_{A_i} + r_{A_k})}{r_{A_i} r_{B_j} r_{A_k}} \\ & + K'^3_{AB} \sum_i \sum_j \sum_k \sum_l \Phi_{A_i} \Phi_{B_j} \Phi_{A_k} \Phi_{B_l} \frac{(r_{A_i} + r_{A_k})}{r_{A_i} r_{B_j} r_{A_k} r_{B_l}} \\ & + K'^4_{AB} \sum_i \sum_j \sum_k \sum_l \sum_m \Phi_{A_i} \Phi_{B_j} \Phi_{A_k} \Phi_{B_l} \Phi_{A_m} \frac{(r_{A_i} + r_{A_k} + r_{A_m})}{r_{A_i} r_{B_j} r_{A_k} r_{B_l} r_{A_m}} + \ldots \\ & + K'_{AB} \sum_i \frac{\Phi_{B_i}}{r_{B_i}} \sum_j \Phi_{A_j} + K'^2_{AB} \sum_i \sum_j \sum_k \Phi_{B_i} \Phi_{A_j} \Phi_{B_k} \frac{r_{A_j}}{r_{B_i} r_{A_j} r_{B_k}} \\ & + K'^3_{AB} \sum_i \sum_j \sum_k \sum_l \Phi_{B_i} \Phi_{A_j} \Phi_{B_k} \Phi_{A_l} \frac{(r_{A_j} + r_{A_l})}{r_{B_i} r_{A_j} r_{B_k} r_{A_l}} \\ & + K'^4_{AB} \sum_i \sum_j \sum_k \sum_l \sum_m \Phi_{B_i} \Phi_{A_j} \Phi_{B_k} \Phi_{A_l} \Phi_{B_m} \frac{(r_{A_j} + r_{A_l})}{r_{B_i} r_{A_j} r_{B_k} r_{A_l} r_{B_m}} + \ldots\end{aligned}$$

$$= \sum_i \Phi_{A_i} + \frac{K'_{AB}}{r_B} \sum_i \Phi_{A_i} \sum_j \frac{\Phi_{B_j}}{j} + \frac{2K'^2_{AB}}{r_A r_B} \sum_i \Phi_{A_i} \sum_j \frac{\Phi_{B_j}}{j} \sum_k \frac{\Phi_{A_k}}{k}$$

$$+ \frac{2K'^3_{AB}}{r_A r_B^2} \sum_i \Phi_{A_i} \sum_j \frac{\Phi_{B_j}}{j} \sum_k \frac{\Phi_{A_k}}{k} \sum_l \frac{\Phi_{B_l}}{l}$$

$$+ \frac{3K'^4_{AB}}{r_A^2 r_B^2} \sum_i \Phi_{A_i} \left(\sum_j \frac{\Phi_{B_j}}{j} \sum_k \frac{\Phi_{A_k}}{k} \right)^2 + \ldots \frac{K'_{AB}}{r_B} \sum_i \Phi_{A_i} \sum_j \frac{\Phi_{B_j}}{j}$$

$$+ \frac{K'^2_{AB}}{r_B^2} \sum_i \Phi_{A_i} \left(\sum_j \frac{\Phi_{B_j}}{j} \right)^2 + \frac{2K'^3_{AB}}{r_A r_B^2} \sum_i \Phi_{A_i} \sum_j \frac{\Phi_{B_j}}{j} \sum_i \frac{\Phi_{A_i}}{i} \sum_j \frac{\Phi_{B_j}}{j}$$

$$+ \frac{2K'^4_{AB}}{r_A r_B^3} \sum_i \Phi_{A_i} \left(\sum_j \frac{\Phi_{B_j}}{j} \right)^2 \sum_j \frac{\Phi_{B_j}}{j} \sum_k \frac{\Phi_{A_k}}{k} + \ldots$$

$$= \bar{S}_A + \frac{K'_{AB}}{r_B} \bar{S}_A S_B + \frac{2K'^2_{AB}}{r_A r_B} \bar{S}_A S_A S_B + \frac{2K'^3_{AB}}{r_A r_B^2} \bar{S}_A S_B S_A S_B$$

$$+ \frac{3K'^4_{AB}}{r_A^2 r_B^2} \bar{S}_A (S_A S_B)^2 + \ldots + \frac{K'_{AB}}{r_B} \bar{S}_A S_B + \frac{K'^2_{AB}}{r_B^2} \bar{S}_A S_B^2$$

$$+ \frac{2K'^3_{AB}}{r_A r_B^2} \bar{S}_A S_B S_A S_B + \frac{2K'^4_{AB}}{r_A r_B^3} \bar{S}_A S_B^2 (S_A S_B) + \ldots \tag{A5}$$

where $\bar{S}_A$, $\bar{S}_B$, S_A and S_B are defined by eqns. (13–16). The following infinite series can be used to summarize terms on the right hand side of eqn. (A5).

$$\frac{2 r_A \bar{S}_A}{K'_{AB} S_A} \sum_i i \left(\frac{K'^2_{AB}}{r_A r_B} S_A S_B \right)^i = \frac{2K'_{AB}}{r_B} \bar{S}_A S_B + \frac{4K'^3_{AB}}{r_A r_B^2} \bar{S}_A S_B (S_A S_B) + \ldots \tag{A6}$$

$$\bar{S}_A \sum_i (i+1) \left(\frac{K'^2_{AB}}{r_A r_B} S_A S_B \right)^i = \frac{2\bar{S}_A K'^2_{AB}}{r_A r_B} S_A S_B + \frac{3\bar{S}_A K'^4_{AB}}{r_A^2 r_B^2} (S_A S_B)^2 + \ldots \tag{A7}$$

$$\frac{\bar{S}_A S_B r_A}{S_A r_B} \sum_i i \left(\frac{K'^2_{AB}}{r_A r_B} S_A S_B \right)^i = \frac{K'^2_{AB}}{r_B^2} \bar{S}_A S_B^2 + \frac{2K'^4_{AB}}{r_A r_B^3} \bar{S}_A S_B^2 (S_A S_B) + \ldots \tag{A8}$$

Performing the summation of eqns. (A6–A8) and inserting derived expressions into eqn. (A5) gives

$$\Phi_A = \bar{S}_A + \frac{r_A}{\left(1 - r_A r_B K^2_{AB} S_A S_B\right)^2} \left[2K_{AB} \bar{S}_A S_B + r_B K^2_{AB} \bar{S}_A S_A S_B \left(2 - r_A r_B K^2_{AB} S_A S_B\right) + r_A K^2_{AB} \bar{S}_A S_B^2 \right] \tag{A9}$$

Similarly, we can derive

$$\Phi_{\mathrm{B}} = \bar{S}_{\mathrm{B}} + \frac{r_{\mathrm{B}}}{\left(1 - r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}}^2 S_{\mathrm{A}} S_{\mathrm{B}}\right)^2} \times \left[2K_{\mathrm{AB}} S_{\mathrm{A}} \bar{S}_{\mathrm{B}} + r_{\mathrm{A}} K_{\mathrm{AB}}^2 S_{\mathrm{A}} \bar{S}_{\mathrm{B}} S_{\mathrm{B}} \left(2 - r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}}^2 S_{\mathrm{A}} S_{\mathrm{B}}\right) + r_{\mathrm{B}} K_{\mathrm{AB}}^2 S_{\mathrm{A}}^2 \bar{S}_{\mathrm{B}}\right] \quad \text{(A10)}$$

Equations (A9) and (A10) are not identical to those based on an assumption of volume change of mixing [25].

Ternary alcohol(A)–alcohol(B)–nonassociating component(C)-mixtures

Φ_{A} is expressed in the same way as described above.

$$\begin{aligned}\Phi_{\mathrm{A}} = {} & \sum_i \Phi_{\mathrm{A}_i} + \sum_i \sum_j \Phi_{\mathrm{A}_i\mathrm{B}_j} \frac{r_{\mathrm{A}_i}}{r_{\mathrm{A}_i\mathrm{B}_j}} + \sum_i \sum_j \sum_k \Phi_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k} \frac{r_{\mathrm{A}_i\mathrm{A}_k}}{r_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k}} \\ & + \sum_i \sum_j \sum_k \sum_l \Phi_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{B}_l} \frac{r_{\mathrm{A}_i\mathrm{A}_k}}{r_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{B}_l}} + \ldots + \sum_i \sum_j \Phi_{\mathrm{B}_i\mathrm{A}_j} \frac{r_{\mathrm{A}_j}}{r_{\mathrm{B}_i\mathrm{A}_j}} \\ & + \sum_i \sum_j \sum_k \Phi_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k} \frac{r_{\mathrm{A}_j}}{r_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k}} + \sum_i \sum_j \sum_k \sum_l \Phi_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{A}_l} \frac{r_{\mathrm{A}_j\mathrm{A}_l}}{r_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{A}_l}} + \ldots \\ & + \sum_i \Phi_{\mathrm{A}_i\mathrm{C}} \frac{r_{\mathrm{A}_i}}{r_{\mathrm{A}_i\mathrm{C}}} + \sum_i \sum_j \Phi_{\mathrm{A}_i\mathrm{B}_j\mathrm{C}} \frac{r_{\mathrm{A}_i}}{r_{\mathrm{A}_i\mathrm{B}_j\mathrm{C}}} + \sum_i \sum_j \sum_k \Phi_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{C}} \frac{r_{\mathrm{A}_i\mathrm{A}_k}}{r_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{C}}} + \ldots \\ & + \sum_i \sum_j \Phi_{\mathrm{B}_i\mathrm{A}_j\mathrm{C}} \frac{r_{\mathrm{A}_j}}{r_{\mathrm{B}_i\mathrm{A}_j\mathrm{C}}} + \sum_i \sum_j \sum_k \Phi_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{C}} \frac{r_{\mathrm{A}_j}}{r_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{C}}} + \ldots \qquad \text{(A11)}\end{aligned}$$

where

$$\sum_i \Phi_{\mathrm{A}_i\mathrm{C}} \frac{r_{\mathrm{A}_i}}{r_{\mathrm{A}_i\mathrm{C}}} = \frac{K'_{\mathrm{AC}} \Phi_{\mathrm{C}_1}}{r_{\mathrm{C}}} \bar{S}_{\mathrm{A}} = r_{\mathrm{A}} K_{\mathrm{AC}} \Phi_{\mathrm{C}_1} \bar{S}_{\mathrm{A}} \qquad \text{(A12)}$$

and

$$\begin{aligned} & \sum_i \sum_j \Phi_{\mathrm{A}_i\mathrm{B}_j\mathrm{C}} \frac{r_{\mathrm{A}_i}}{r_{\mathrm{A}_i\mathrm{B}_j\mathrm{C}}} + \sum_i \sum_j \sum_k \Phi_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{C}} \frac{r_{\mathrm{A}_i\mathrm{A}_k}}{r_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{C}}} \\ & + \sum_i \sum_j \sum_k \sum_l \Phi_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{B}_l\mathrm{C}} \frac{r_{\mathrm{A}_i\mathrm{A}_k}}{r_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{B}_l\mathrm{C}}} + \ldots \\ & + \sum_i \sum_j \Phi_{\mathrm{B}_i\mathrm{A}_j\mathrm{C}} \frac{r_{\mathrm{A}_j}}{r_{\mathrm{B}_i\mathrm{A}_j\mathrm{C}}} + \sum_i \sum_j \sum_k \Phi_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{C}} \frac{r_{\mathrm{A}_j}}{r_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{C}}} \\ & + \sum_i \sum_j \sum_k \sum_l \Phi_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{A}_l\mathrm{C}} \frac{r_{\mathrm{A}_j\mathrm{A}_l}}{r_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{A}_l\mathrm{C}}} + \ldots \\ & = \frac{K'_{\mathrm{BC}} \Phi_{\mathrm{C}_1} K'_{\mathrm{AB}}}{r_{\mathrm{C}} r_{\mathrm{B}}} \sum_i \Phi_{\mathrm{A}_i} \sum_j \frac{\Phi_{\mathrm{B}_j}}{j} + \frac{K'_{\mathrm{AC}} \Phi_{\mathrm{C}_1} K'^2_{\mathrm{AB}}}{r_{\mathrm{C}}} \sum_i \sum_j \sum_k \Phi_{\mathrm{A}_i} \Phi_{\mathrm{B}_j} \Phi_{\mathrm{A}_k} \frac{\left(r_{\mathrm{A}_i} + r_{\mathrm{A}_k}\right)}{r_{\mathrm{A}_i} r_{\mathrm{B}_j} r_{\mathrm{A}_k}} \end{aligned}$$

$$+\frac{K'_{\mathrm{BC}}\Phi_{\mathrm{C}_1}K'^{3}_{\mathrm{AB}}}{r_{\mathrm{C}}}\sum_i\sum_j\sum_k\sum_l\Phi_{\mathrm{A}_i}\Phi_{\mathrm{B}_j}\Phi_{\mathrm{A}_k}\Phi_{\mathrm{B}_l}\frac{(r_{\mathrm{A}_i}+r_{\mathrm{A}_k})}{r_{\mathrm{A}_i}r_{\mathrm{B}_j}r_{\mathrm{A}_k}r_{\mathrm{B}_l}}+\ldots$$

$$+\frac{K'_{\mathrm{AC}}\Phi_{\mathrm{C}_1}K'_{\mathrm{AB}}}{r_{\mathrm{C}}r_{\mathrm{B}}}\sum_i\Phi_{\mathrm{A}_i}\sum_j\frac{\Phi_{\mathrm{B}_j}}{j}$$

$$+\frac{K'_{\mathrm{BC}}\Phi_{\mathrm{C}_1}K'^{2}_{\mathrm{AB}}}{r_{\mathrm{C}}}\sum_i\sum_j\sum_k\Phi_{\mathrm{B}_i}\Phi_{\mathrm{A}_j}\Phi_{\mathrm{B}_k}\frac{r_{\mathrm{A}_j}}{r_{\mathrm{B}_i}r_{\mathrm{A}_j}r_{\mathrm{B}_k}}$$

$$+\frac{K'_{\mathrm{AC}}\Phi_{\mathrm{C}_1}K'^{3}_{\mathrm{AB}}}{r_{\mathrm{C}}}\sum_i\sum_j\sum_k\sum_l\Phi_{\mathrm{B}_i}\Phi_{\mathrm{A}_j}\Phi_{\mathrm{B}_k}\Phi_{\mathrm{A}_l}\frac{(r_{\mathrm{A}_j}+r_{\mathrm{A}_l})}{r_{\mathrm{B}_i}r_{\mathrm{A}_j}r_{\mathrm{B}_k}r_{\mathrm{A}_l}}+\ldots$$

$$=\frac{\Phi_{\mathrm{C}_1}}{r_{\mathrm{C}}}\left[\frac{K'_{\mathrm{BC}}K'_{\mathrm{AB}}}{r_{\mathrm{B}}}\sum_i\Phi_{\mathrm{A}_i}\sum_j\frac{\Phi_{\mathrm{B}_j}}{j}+\frac{2K'_{\mathrm{AC}}K'^{2}_{\mathrm{AB}}}{r_{\mathrm{A}}r_{\mathrm{B}}}\sum_i\Phi_{\mathrm{A}_i}\sum_j\frac{\Phi_{\mathrm{B}_j}}{j}\sum_k\frac{\Phi_{\mathrm{A}_k}}{k}\right.$$

$$+\frac{2K'_{\mathrm{BC}}K'^{3}_{\mathrm{AB}}}{r_{\mathrm{A}}r_{\mathrm{B}}^{2}}\sum_i\Phi_{\mathrm{A}_i}\sum_j\frac{\Phi_{\mathrm{B}_j}}{j}\sum_k\frac{\Phi_{\mathrm{A}_k}}{k}\sum_l\frac{\Phi_{\mathrm{B}_l}}{l}$$

$$+\frac{3K'_{\mathrm{AC}}K'^{4}_{\mathrm{AB}}}{r_{\mathrm{A}}^{2}r_{\mathrm{B}}^{2}}\sum_i\Phi_{\mathrm{A}_i}\sum_j\frac{\Phi_{\mathrm{B}_j}}{j}\sum_k\frac{\Phi_{\mathrm{A}_k}}{k}\sum_l\frac{\Phi_{\mathrm{B}_l}}{l}\sum_m\frac{\Phi_{\mathrm{A}_m}}{m}+\ldots$$

$$+\frac{K'_{\mathrm{AC}}K'_{\mathrm{AB}}}{r_{\mathrm{B}}}\sum_i\frac{\Phi_{\mathrm{B}_i}}{i}\sum_j\Phi_{\mathrm{A}_j}+\frac{K'_{\mathrm{BC}}K'^{2}_{\mathrm{AB}}}{r_{\mathrm{B}}^{2}}\sum_i\frac{\Phi_{\mathrm{B}_i}}{i}\sum_j\Phi_{\mathrm{A}_j}\sum_k\frac{\Phi_{\mathrm{B}_k}}{k}$$

$$+\frac{2K'_{\mathrm{AC}}K'^{3}_{\mathrm{AB}}}{r_{\mathrm{A}}r_{\mathrm{B}}^{2}}\sum_i\frac{\Phi_{\mathrm{B}_i}}{i}\sum_j\Phi_{\mathrm{A}_j}\sum_k\frac{\Phi_{\mathrm{B}_k}}{k}\sum_l\frac{\Phi_{\mathrm{A}_l}}{l}$$

$$\left.+\frac{2K'_{\mathrm{BC}}K'^{4}_{\mathrm{AB}}}{r_{\mathrm{A}}r_{\mathrm{B}}^{3}}\sum_i\frac{\Phi_{\mathrm{B}_i}}{i}\sum_j\Phi_{\mathrm{A}_j}\sum_k\frac{\Phi_{\mathrm{B}_k}}{k}\sum_l\frac{\Phi_{\mathrm{A}_l}}{l}\sum_m\frac{\Phi_{\mathrm{B}_m}}{m}+\ldots\right]$$

$$=\frac{\Phi_{\mathrm{C}_1}}{r_{\mathrm{C}}}\left[\frac{K'_{\mathrm{BC}}K'_{\mathrm{AB}}}{r_{\mathrm{B}}}\bar{S}_{\mathrm{A}}S_{\mathrm{B}}+\frac{2K'_{\mathrm{AC}}K'^{2}_{\mathrm{AB}}}{r_{\mathrm{A}}r_{\mathrm{B}}}\bar{S}_{\mathrm{A}}(S_{\mathrm{A}}S_{\mathrm{B}})+\frac{2K'_{\mathrm{BC}}K'^{3}_{\mathrm{AB}}}{r_{\mathrm{A}}r_{\mathrm{B}}^{2}}\bar{S}_{\mathrm{A}}S_{\mathrm{B}}(S_{\mathrm{A}}S_{\mathrm{B}})\right.$$

$$+\frac{3K'_{\mathrm{AC}}K'^{4}_{\mathrm{AB}}}{r_{\mathrm{A}}^{2}r_{\mathrm{B}}^{2}}\bar{S}_{\mathrm{A}}(S_{\mathrm{A}}S_{\mathrm{B}})^{2}+\ldots$$

$$+\frac{K'_{\mathrm{AC}}K'_{\mathrm{AB}}}{r_{\mathrm{B}}}\bar{S}_{\mathrm{A}}S_{\mathrm{B}}+\frac{K'_{\mathrm{BC}}K'^{2}_{\mathrm{AB}}}{r_{\mathrm{B}}^{2}}\bar{S}_{\mathrm{A}}S_{\mathrm{B}}^{2}+\frac{2K'_{\mathrm{AC}}K'^{3}_{\mathrm{AB}}}{r_{\mathrm{A}}r_{\mathrm{B}}^{2}}\bar{S}_{\mathrm{A}}S_{\mathrm{B}}(S_{\mathrm{A}}S_{\mathrm{B}})$$

$$\left.+\frac{2K'_{\mathrm{BC}}K'^{4}_{\mathrm{AB}}}{r_{\mathrm{A}}r_{\mathrm{B}}^{3}}\bar{S}_{\mathrm{A}}S_{\mathrm{B}}^{2}(S_{\mathrm{A}}S_{\mathrm{B}})+\ldots\right]$$

$$=\frac{\Phi_{\mathrm{C}_1}}{r_{\mathrm{C}}}\left[\frac{(K'_{\mathrm{AC}}+K'_{\mathrm{BC}})}{K'_{\mathrm{AB}}}\frac{\bar{S}_{\mathrm{A}}r_{\mathrm{A}}}{S_{\mathrm{A}}}\sum_i i\left(\frac{K'^{2}_{\mathrm{AB}}}{r_{\mathrm{A}}r_{\mathrm{B}}}S_{\mathrm{A}}S_{\mathrm{B}}\right)^{i}\right.$$

$$\left.+K'_{\mathrm{AC}}\bar{S}_{\mathrm{A}}\sum_i(i+1)\left(\frac{K'^{2}_{\mathrm{AB}}}{r_{\mathrm{A}}r_{\mathrm{B}}}S_{\mathrm{A}}S_{\mathrm{B}}\right)^{i}+\frac{K'_{\mathrm{BC}}\bar{S}_{\mathrm{A}}S_{\mathrm{B}}r_{\mathrm{A}}}{S_{\mathrm{A}}r_{\mathrm{B}}}\sum_i i\left(\frac{K'^{2}_{\mathrm{AB}}}{r_{\mathrm{A}}r_{\mathrm{B}}}S_{\mathrm{A}}S_{\mathrm{B}}\right)^{i}\right]$$

$$= \frac{\Phi_{C_1}}{r_C\left(1 - \frac{K'^2_{AB}}{r_A r_B} S_A S_B\right)^2} \left[(K'_{AC} + K'_{BC}) \frac{K'_{AB}}{r_B} \bar{S}_A S_B \right.$$

$$\left. + \frac{K'^2_{AB} K'_{AC}}{r_A r_B} \bar{S}_A S_A S_B \left(2 - \frac{K'^2_{AB}}{r_A r_B} S_A S_B\right) + \frac{K'^2_{AB} K'_{BC}}{r_B^2} \bar{S}_A S_B^2 \right] \tag{A13}$$

where $K'_{AC} = r_A r_C K_{AC}$ and $K'_{BC} = r_B r_C K_{BC}$.

Since the summation of the other terms on the right hand side of eqn. (A11) is described in eqn. (A9), Φ_A is given by

$$\Phi_A = (1 + r_A K_{AC} \Phi_{C_1}) \bar{S}_A + \frac{r_A}{(1 - r_A r_B K_{AB}^2 S_A S_B)^2}$$
$$\times \left[2K_{AB} \bar{S}_A S_B + r_B K_{AB}^2 \bar{S}_A S_A S_B (2 - r_A r_B K_{AB}^2 S_A S_B) \right.$$
$$+ r_A K_{AB}^2 \bar{S}_A S_B^2 + \Phi_{C_1} \{ (r_A K_{AC} + r_B K_{BC}) K_{AB} \bar{S}_A S_B$$
$$\left. + r_A r_B K_{AB}^2 K_{AC} \bar{S}_A S_A S_B (2 - r_A r_B K_{AB}^2 S_A S_B) + r_A r_B K_{AB}^2 K_{BC} \bar{S}_A S_B^2 \} \right] \tag{A14}$$

Similarly, we can derive Φ_B and Φ_C as follows

$$\Phi_B = (1 + r_B K_{BC} \Phi_{C_1}) \bar{S}_B + \frac{r_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)^2}$$
$$\times \left[2K_{AB} S_A \bar{S}_B + r_A K_{AB}^2 S_A \bar{S}_B S_B (2 - r_A r_B K_{AB}^2 S_A S_B) \right.$$
$$+ r_B K_{AB}^2 S_A^2 \bar{S}_B + \Phi_{C_1} \{ (r_A K_{AC} + r_B K_{BC}) K_{AB} S_A \bar{S}_B$$
$$\left. + r_A r_B K_{AB}^2 K_{BC} S_A \bar{S}_B S_B (2 - r_A r_B K_{AB}^2 S_A S_B) + r_A r_B K_{AB}^2 K_{AC} S_A^2 \bar{S}_B \} \right] \tag{A15}$$

$$\Phi_C = \Phi_{C_1} \left[1 + r_C K_{AC} S_A + r_C K_{BC} S_B + \frac{r_A r_B r_C K_{AB}^2 S_A S_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)} \right.$$
$$\left. \times \left(\frac{K_{AC}}{r_B K_{AB}} + \frac{K_{BC}}{r_A K_{AB}} + K_{AC} S_A + K_{BC} S_B \right) \right] \tag{A16}$$

APPENDIX B

DERIVATION OF THE EXPRESSION FOR THE TRUE MOLAR VOLUME

Binary alcohol(A)–alcohol(B)-mixtures

The true molar volume is expressed by

$$\frac{1}{V} = \sum_i \frac{\Phi_{A_i}}{r_{A_i}} + \sum_i \frac{\Phi_{B_i}}{r_{B_i}} + \sum_i \sum_j \frac{\Phi_{A_i B_j}}{r_{A_i B_j}} + \sum_i \sum_j \sum_k \frac{\Phi_{A_i B_j A_k}}{r_{A_i B_j A_k}} + \sum_i \sum_j \sum_k \sum_l \frac{\Phi_{A_i B_j A_k B_l}}{r_{A_i B_j A_k B_l}}$$

$$+\sum_{i}\sum_{j}\sum_{k}\sum_{l}\sum_{m}\frac{\Phi_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{B}_l\mathrm{A}_m}}{r_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{B}_l\mathrm{A}_m}}+\ldots$$

$$+\sum_{i}\sum_{j}\frac{\Phi_{\mathrm{B}_i\mathrm{A}_j}}{r_{\mathrm{B}_i\mathrm{A}_j}}+\sum_{i}\sum_{j}\sum_{k}\frac{\Phi_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k}}{r_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k}}+\sum_{i}\sum_{j}\sum_{k}\sum_{l}\frac{\Phi_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{A}_l}}{r_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{A}_l}}$$

$$+\sum_{i}\sum_{j}\sum_{k}\sum_{l}\sum_{m}\frac{\Phi_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{A}_l\mathrm{B}_m}}{r_{\mathrm{B}_i\mathrm{A}_j\mathrm{B}_k\mathrm{A}_l\mathrm{B}_m}}+\ldots$$

$$=\frac{1}{r_{\mathrm{A}}}\sum_{i}\frac{\Phi_{\mathrm{A}_i}}{i}+\frac{1}{r_{\mathrm{B}}}\sum_{i}\frac{\Phi_{\mathrm{B}_i}}{i}+\frac{K'_{\mathrm{AB}}}{r_{\mathrm{A}}r_{\mathrm{B}}}\sum_{i}\frac{\Phi_{\mathrm{A}_i}}{i}\sum_{j}\frac{\Phi_{\mathrm{B}_j}}{j}$$

$$+\frac{K'^2_{\mathrm{AB}}}{r_{\mathrm{A}}^2r_{\mathrm{B}}}\sum_{i}\frac{\Phi_{\mathrm{A}_i}}{i}\sum_{j}\frac{\Phi_{\mathrm{B}_j}}{j}\sum_{k}\frac{\Phi_{\mathrm{A}_k}}{k}+\frac{K'^3_{\mathrm{AB}}}{r_{\mathrm{A}}^2r_{\mathrm{B}}^2}\sum_{i}\frac{\Phi_{\mathrm{A}_i}}{i}\sum_{j}\frac{\Phi_{\mathrm{B}_j}}{j}\sum_{k}\frac{\Phi_{\mathrm{A}_k}}{k}\sum_{l}\frac{\Phi_{\mathrm{B}_l}}{l}$$

$$+\frac{K'^4_{\mathrm{AB}}}{r_{\mathrm{A}}^3r_{\mathrm{B}}^2}\sum_{i}\frac{\Phi_{\mathrm{A}_i}}{i}\sum_{j}\frac{\Phi_{\mathrm{B}_j}}{j}\sum_{k}\frac{\Phi_{\mathrm{A}_k}}{k}\sum_{l}\frac{\Phi_{\mathrm{B}_l}}{l}\sum_{m}\frac{\Phi_{\mathrm{A}_m}}{m}+\ldots$$

$$+\frac{K'_{\mathrm{AB}}}{r_{\mathrm{A}}r_{\mathrm{B}}}\sum_{i}\frac{\Phi_{\mathrm{B}_i}}{i}\sum_{j}\frac{\Phi_{\mathrm{A}_j}}{j}+\frac{K'^2_{\mathrm{AB}}}{r_{\mathrm{B}}^2r_{\mathrm{A}}}\sum_{i}\frac{\Phi_{\mathrm{B}_i}}{i}\sum_{j}\frac{\Phi_{\mathrm{A}_j}}{j}\sum_{k}\frac{\Phi_{\mathrm{B}_k}}{k}$$

$$+\frac{K'^3_{\mathrm{AB}}}{r_{\mathrm{B}}^2r_{\mathrm{A}}^2}\sum_{i}\frac{\Phi_{\mathrm{B}_i}}{i}\sum_{j}\frac{\Phi_{\mathrm{A}_j}}{j}\sum_{k}\frac{\Phi_{\mathrm{B}_k}}{k}\sum_{l}\frac{\Phi_{\mathrm{A}_l}}{l}$$

$$+\frac{K'^4_{\mathrm{AB}}}{r_{\mathrm{B}}^3r_{\mathrm{A}}^2}\sum_{i}\frac{\Phi_{\mathrm{B}_i}}{i}\sum_{j}\frac{\Phi_{\mathrm{A}_j}}{j}\sum_{k}\frac{\Phi_{\mathrm{B}_k}}{k}\sum_{l}\frac{\Phi_{\mathrm{A}_l}}{l}\sum_{m}\frac{\Phi_{\mathrm{B}_m}}{m}+\ldots$$

$$=\frac{S_{\mathrm{A}}}{r_{\mathrm{A}}}+\frac{S_{\mathrm{B}}}{r_{\mathrm{B}}}+\frac{K'_{\mathrm{AB}}}{r_{\mathrm{A}}r_{\mathrm{B}}}S_{\mathrm{A}}S_{\mathrm{B}}\left[+\frac{K'^2_{\mathrm{AB}}}{r_{\mathrm{A}}^2r_{\mathrm{B}}}S_{\mathrm{A}}S_{\mathrm{B}}S_{\mathrm{A}}\right]+\frac{K'^3_{\mathrm{AB}}}{r_{\mathrm{A}}^2r_{\mathrm{B}}^2}(S_{\mathrm{A}}S_{\mathrm{B}})^2$$

$$+\frac{K'^4_{\mathrm{AB}}}{r_{\mathrm{A}}^3r_{\mathrm{B}}^2}S_{\mathrm{A}}(S_{\mathrm{A}}S_{\mathrm{B}})^2+\ldots+\frac{K'_{\mathrm{AB}}}{r_{\mathrm{B}}r_{\mathrm{A}}}S_{\mathrm{B}}S_{\mathrm{A}}+\frac{K'^2_{\mathrm{AB}}}{r_{\mathrm{B}}^2r_{\mathrm{A}}}S_{\mathrm{B}}S_{\mathrm{A}}S_{\mathrm{B}}$$

$$+\frac{K'^3_{\mathrm{AB}}}{r_{\mathrm{B}}^2r_{\mathrm{A}}^2}(S_{\mathrm{B}}S_{\mathrm{A}})^2+\frac{K'^4_{\mathrm{AB}}}{r_{\mathrm{B}}^3r_{\mathrm{A}}^2}S_{\mathrm{B}}(S_{\mathrm{A}}S_{\mathrm{B}})^2+\ldots$$

$$=\frac{S_{\mathrm{A}}}{r_{\mathrm{A}}}+\frac{S_{\mathrm{B}}}{r_{\mathrm{B}}}+\left(\frac{2}{K'_{\mathrm{AB}}}+\frac{S_{\mathrm{A}}}{r_{\mathrm{A}}}+\frac{S_{\mathrm{B}}}{r_{\mathrm{B}}}\right)\sum_{i}\left(\frac{K'^2_{\mathrm{AB}}}{r_{\mathrm{A}}r_{\mathrm{B}}}S_{\mathrm{A}}S_{\mathrm{B}}\right)^{i}$$

$$=\frac{S_{\mathrm{A}}}{r_{\mathrm{A}}}+\frac{S_{\mathrm{B}}}{r_{\mathrm{B}}}+\frac{r_{\mathrm{A}}r_{\mathrm{B}}K^2_{\mathrm{AB}}S_{\mathrm{A}}S_{\mathrm{B}}}{(1-r_{\mathrm{A}}r_{\mathrm{B}}K^2_{\mathrm{AB}}S_{\mathrm{A}}S_{\mathrm{B}})}\left(\frac{2}{r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}}+\frac{S_{\mathrm{A}}}{r_{\mathrm{A}}}+\frac{S_{\mathrm{B}}}{r_{\mathrm{B}}}\right) \tag{B1}$$

Ternary alcohol(A)–alcohol(B)–nonassociating component(C)-mixtures

$1/V$ is given by

$$\begin{aligned}
\frac{1}{V} &= \sum_i \frac{\Phi_{A_i}}{r_{A_i}} + \sum_i \frac{\Phi_{B_i}}{r_{B_i}} + \sum_i \sum_j \frac{\Phi_{A_iB_j}}{r_{A_iB_j}} + \sum_i \sum_j \sum_k \frac{\Phi_{A_iB_jA_k}}{r_{A_iB_jA_k}} \\
&\quad + \sum_i \sum_j \sum_k \sum_l \frac{\Phi_{A_iB_jA_kB_l}}{r_{A_iB_jA_kB_l}} + \sum_i \sum_j \sum_k \sum_l \sum_m \frac{\Phi_{A_iB_jA_kB_lA_m}}{r_{A_iB_jA_kB_lA_m}} + \dots \\
&\quad + \sum_i \sum_j \frac{\Phi_{B_iA_j}}{r_{B_iA_j}} + \sum_i \sum_j \sum_k \frac{\Phi_{B_iA_jB_k}}{r_{B_iA_jB_k}} + \sum_i \sum_j \sum_k \sum_l \frac{\Phi_{B_iA_jB_kA_l}}{r_{B_iA_jB_kA_l}} \\
&\quad + \sum_i \sum_j \sum_k \sum_l \sum_m \frac{\Phi_{B_iA_jB_kA_lB_m}}{r_{B_iA_jB_kA_lB_m}} + \dots \\
&\quad + \frac{\Phi_{C_1}}{r_C} + \sum_i \frac{\Phi_{A_iC}}{r_{A_iC}} + \sum_i \frac{\Phi_{B_iC}}{r_{B_iC}} + \sum_i \sum_j \frac{\Phi_{A_iB_jC}}{r_{A_iB_jC}} \\
&\quad + \sum_i \sum_j \sum_k \frac{\Phi_{A_iB_jA_kC}}{r_{A_iB_jA_kC}} + \sum_i \sum_j \sum_k \sum_l \frac{\Phi_{A_iB_jA_kB_lC}}{r_{A_iB_jA_kB_lC}} + \dots \\
&\quad + \sum_i \sum_j \frac{\Phi_{B_iA_jC}}{r_{B_iA_jC}} + \sum_i \sum_j \sum_k \frac{\Phi_{B_iA_jB_kC}}{r_{B_iA_jB_kC}} + \sum_i \sum_j \sum_k \sum_l \frac{\Phi_{B_iA_jB_kA_lC}}{r_{B_iA_jB_kA_lC}} + \dots
\end{aligned} \tag{B2}$$

where

$$\sum_i \frac{\Phi_{A_iC}}{r_{A_iC}} = \frac{K'_{AC}\Phi_{C_1}}{r_C} \sum_i \frac{\Phi_{A_i}}{r_{A_i}} = K_{AC}\Phi_{C_1}S_A \tag{B3}$$

$$\sum_i \frac{\Phi_{B_iC}}{r_{B_iC}} = K_{BC}\Phi_{C_1}S_B \tag{B4}$$

$$\begin{aligned}
&\sum_i \sum_j \frac{\Phi_{A_iB_jC}}{r_{A_iB_jC}} + \sum_i \sum_j \sum_k \frac{\Phi_{A_iB_jA_kC}}{r_{A_iB_jA_kC}} + \sum_i \sum_j \sum_k \sum_l \frac{\Phi_{A_iB_jA_kB_lC}}{r_{A_iB_jA_kB_lC}} \\
&\quad + \sum_i \sum_j \sum_k \sum_l \sum_m \frac{\Phi_{A_iB_jA_kB_lA_mC}}{r_{A_iB_jA_kB_lA_mC}} + \dots \\
&\quad + \sum_i \sum_j \frac{\Phi_{B_iA_jC}}{r_{B_iA_jC}} + \sum_i \sum_j \sum_k \frac{\Phi_{B_iA_jB_kC}}{r_{B_iA_jB_kC}} + \sum_i \sum_j \sum_k \sum_l \frac{\Phi_{B_iA_jB_kA_lC}}{r_{B_iA_jB_kA_lC}} \\
&\quad + \sum_i \sum_j \sum_k \sum_l \sum_m \frac{\Phi_{B_iA_jB_kA_lB_mC}}{r_{B_iA_jB_kA_lB_mC}} + \dots
\end{aligned}$$

$$
\begin{aligned}
&= \frac{\Phi_{C_1}}{r_C}\left[\frac{K'_{BC}K'_{AB}}{r_A r_B}\sum_i \frac{\Phi_{A_i}}{i}\sum_j \frac{\Phi_{B_j}}{j} + \frac{K'_{AC}K'^2_{AB}}{r_A^2 r_B}\sum_i \frac{\Phi_{A_i}}{i}\sum_j \frac{\Phi_{B_j}}{j}\sum_k \frac{\Phi_{A_k}}{k}\right. \\
&\quad + \frac{K'_{BC}K'^3_{AB}}{r_A^2 r_B^2}\sum_i \frac{\Phi_{A_i}}{i}\sum_j \frac{\Phi_{B_j}}{j}\sum_k \frac{\Phi_{A_k}}{k}\sum_l \frac{\Phi_{B_l}}{l} \\
&\quad + \frac{K'_{AC}K'^4_{AB}}{r_A^3 r_B^2}\sum_i \frac{\Phi_{A_i}}{i}\sum_j \frac{\Phi_{B_j}}{j}\sum_k \frac{\Phi_{A_k}}{k}\sum_l \frac{\Phi_{B_l}}{l}\sum_m \frac{\Phi_{A_m}}{m} + \dots \\
&\quad + \frac{K'_{AC}K'_{AB}}{r_B r_A}\sum_i \frac{\Phi_{B_i}}{i}\sum_j \frac{\Phi_{A_j}}{j} + \frac{K'_{BC}K'^2_{AB}}{r_B^2 r_A}\sum_i \frac{\Phi_{B_i}}{i}\sum_j \frac{\Phi_{A_j}}{j}\sum_k \frac{\Phi_{B_k}}{k} \\
&\quad + \frac{K'_{AC}K'^3_{AB}}{r_B^2 r_A^2}\sum_i \frac{\Phi_{B_i}}{i}\sum_j \frac{\Phi_{A_j}}{j}\sum_k \frac{\Phi_{B_k}}{k}\sum_l \frac{\Phi_{A_l}}{l} \\
&\quad \left. + \frac{K'_{BC}K'^4_{AB}}{r_B^3 r_A^2}\sum_i \frac{\Phi_{B_i}}{i}\sum_j \frac{\Phi_{A_j}}{j}\sum_k \frac{\Phi_{B_k}}{k}\sum_l \frac{\Phi_{A_l}}{l}\sum_m \frac{\Phi_{B_m}}{m} + \dots\right] \\
&= \frac{\Phi_{C_1}}{r_C}\left(\frac{K'_{BC}}{K'_{AB}} + \frac{K'_{AC}}{K'_{AB}} + \frac{K'_{AC}S_A}{r_A} + \frac{K'_{BC}S_B}{r_B}\right)\sum_i\left(\frac{K'^2_{AB}}{r_A r_B}S_A S_B\right)^i \\
&= \Phi_{C_1}\left(\frac{K_{BC}}{r_A K_{AB}} + \frac{K_{AC}}{r_B K_{AB}} + K_{AC}S_A + K_{BC}S_B\right)\frac{r_A r_B K^2_{AB}S_A S_B}{\left(1 - r_A r_B K^2_{AB}S_A S_B\right)}
\end{aligned}
\tag{B5}
$$

Inserting eqns. (B1), (B3)–(B5) into eqn. (B2) yields

$$
\begin{aligned}
\frac{1}{V} &= \frac{S_A}{r_A} + \frac{S_B}{r_B} + \left(\frac{2}{r_A r_B K_{AB}} + \frac{S_A}{r_A} + \frac{S_B}{r_B}\right)\frac{r_A r_B K^2_{AB}S_A S_B}{\left(1 - r_A r_B K^2_{AB}S_A S_B\right)} \\
&\quad + \frac{\Phi_{C_1}}{r_C}\left[1 + r_C K_{AC}S_A + r_C K_{BC}S_B\right. \\
&\quad \left. + \left(\frac{K_{AC}}{r_B K_{AB}} + K_{AC}S_A + \frac{K_{BC}}{r_A K_{AB}} + K_{BC}S_B\right)\frac{r_A r_B r_C K^2_{AB}S_A S_B}{\left(1 - r_A r_B K^2_{AB}S_A S_B\right)}\right]
\end{aligned}
\tag{B6}
$$

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