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THE UNIQUAC ASSOCIATED-SOLUTION MODEL. EXCESS ENTHALPIES OF MIXTURES OF HYDROCARBONS WITH ALCOHOL

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ABSTRACT

Brandani's method is applied to calculate the dimerization constant and the constant for formation of higher polymers from the experimental vapor pressures of alcohols as a function of temperature. The pure-alcohol association constants and a single value of -23.2 kJ mol^{-1} for the enthalpy of a hydrogen bond with the UNIQUAC associated-solution model have been used to correlate binary excess enthalpies for alcohol–hydrocarbon mixtures and to predict ternary excess enthalpies for mixtures of one alcohol with two hydrocarbons.

INTRODUCTION

The UNIQUAC associated-solution model has been successfully used to correlate binary excess enthalpies and to predict ternary excess enthalpies for alcohol–hydrocarbon mixtures [1–3] using the pure-alcohol association constants obtained from binary data reduction. Recently, Brandani [4] presented a method for determining the enthalpy of hydrogen-bond formation and the equilibrium self-association constant for pure liquids, using the fact that the equilibrium constant should be a property of the associating component. In this work, the two equilibrium constants of dimerization and of higher polymerization for pure alcohols have been obtained from the experimental vapor pressures of the pure alcohols as a function of temperature using Brandani's method and we present calculated results for the excess enthalpies of alcohol–hydrocarbon mixtures derived from the UNIQUAC associated-solution model with the new values of the two association constants.

DETERMINATION OF THE ASSOCIATION CONSTANTS

In a previous paper [3], the two-constant UNIQUAC associated-solution model, where only the alcohol dimerization constant for $A_1 + A_1 = A_2$ is

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different and the other alcohol association constants for $A_1 + A_i = A_{i+1}$ ($i = 2, 3$, etc.) are equal, has given improved calculated results in ternary excess enthalpy prediction for mixtures including one aliphatic alcohol and two hydrocarbons than does the one-constant UNIQUAC associated-solution model where only a single value of the equilibrium constant is used. The new values of these two association constants are obtained from pure-alcohol vapor pressure data.

According to Brandani's method [4], the vapor pressure for the alcohol liquids is calculated by

$$P_A^s = \gamma_{A_1}^* x_{A_1}^* P_h^s \exp\left[\left(P_A^s - P_h^s\right)\left(v_A^L - B_A^F\right)/RT\right] \tag{1}$$

where $\gamma_{A_1}^*$ is the activity coefficient of the the monomer adjusted to zero pressure. $x_{A_1}^*$ is the mole fraction of the monomer in the pure-alcohol liquid. P_h^s is the vapor pressure of the hypothetical fluid, v_A^L is the molar pure-alcohol liquid volume calculated from the modified Rackett equation [5], B_A^F is the free molecule contribution to the second virial coefficient and is calculated from the correlation of Hayden and O'Connell [6] with the pertinent parameters given by Prausnitz et al. [7].

The Riedel–Plank–Miller vapor pressure equation [8] is used to calculate P_h^s in terms of $\Theta_h = T_h^b / T_h^c$ and P_h^c, where T_h^b is the normal boiling point of the hypothetical fluid. These parameters required for calculating P_h^s are estimated from the homomorph concept that the homomorph should have the same molar volume as that of the alcohol, as well as a similar molecular structure. The homomorph parameters, Θ_h, T_h^c, and P_h^c, were taken from Brandani [4].

ln $\gamma_{A_1}^*$ is given by

$$\ln \gamma_{A_1}^* = \ln \frac{\phi_{A_1}^*}{x_{A_1}^*} + 1 - \frac{\phi_{A_1}^*}{x_{A_1}^*} \tag{2}$$

where $\phi_{A_1}^*$ is obtained from eqn. (3).

$$\phi_{A_1}^* + \frac{K_2 \phi_{A_1}^{*2}\left(2 - K_A \phi_{A_1}^*\right)}{\left(1 - K_A \phi_{A_1}^*\right)^2} = 1 \tag{3}$$

and $x_{A_1}^*$ is calculated from

$$x_{A_1}^* = \frac{\left(1 - K_A \phi_{A_1}^*\right)}{\left[\left(K_2 - K_A\right)\phi_{A_1}^* + 1\right]} \tag{4}$$

The equilibrium constants, K_2 for dimerization and K_A for polymerization, are defined as follows

$$K_2 = \frac{\phi_{A_2}^*}{2\phi_{A_1}^{*2}} \tag{5}$$

$$K_A = \frac{\phi_{A_{i+1}}^*}{\phi_{A_i}^* \phi_{A_1}^*} \frac{i}{i+1} \quad (i > 1) \tag{6}$$

TABLE 1

Results obtained from vapor-pressure data for alcohols

Substance	Temp. range (°C)	Abs. arith. mean deviation (Torr)
Methanol	−44.0–49.9	0.063
Ethanol	−31.3–63.5	0.32
1-Propanol	−15.0–97.8	0.15
2-Propanol	−26.1–67.8	0.23
1-Butanol	−1.2–117.5	0.66
1-Pentanol	13.6–137.8	0.95
1-Hexanol	24.4–157.0	0.69
1-Heptanol	42.4–175.8	0.30
1-Octanol	54.0–195.2	0.59
1-Decanol	69.5–231.0	1.55

The enthalpies of formation of a hydrogen bond, h_2 and h_A, are assumed to be independent of temperature and fix the temperature dependence of the association constants, K_2 and K_A, according to the van't Hoff relation.

We calculated h_2, h_A, K_2 and K_A for ten aliphatic alcohols by minimizing the following objective function

$$F = \sum_{i=1}^{N} \left[P^s_{A_i}(\mathrm{exp}) - P^s_{A_i}(\mathrm{calc}) \right]^2 \tag{7}$$

where P^s_h was calculated from eqn. (1) and the experimental pure vapor pressure data were obtained from Liley et al. [9]. Table 1 summarizes the temperature range of the experimental data and the absolute arithmetical

TABLE 2

Association and structural parameters for alcohols

Substance	K_2	K_A	$-h_2$	$-h_A$	r	q
	at 50°C		(kJ mol^{-1})			
Methanol	52.9	192.9	27.32	26.78	1.15	1.12
Ethanol	41.6	113.6	28.16	25.27	1.69	1.55
1-Propanol	24.0	95.0	26.61	25.61	2.23	1.98
2-Propanol	24.4	53.0	27.53	24.69	2.23	1.98
1-Butanol	29.4	72.0	26.98	24.98	2.77	2.42
1-Pentanol	26.7	51.5	27.07	22.43	3.31	2.85
1-Hexanol	22.7	44.7	23.81	23.43	3.85	3.28
1-Heptanol	20.8	41.5	24.02	23.39	4.39	3.71
1-Octanol	25.2	48.4	23.18	21.88	4.94	4.15
1-Decanol	20.8	42.1	22.05	18.03	6.01	5.01

mean deviation between calculated and experimental vapor pressures and Table 2 gives the association parameters, together with molecular structural parameters calculated by Vera et al. [10]. The average value of h_2 is -25.7 kJ mol^{-1} and that of h_A is -23.6 kJ mol^{-1}, which agrees with the enthalpy of dilution of ethanol in saturated hydrocarbons measured by Stokes and Burfitt [11] at 25°C.

EXCESS ENTHALPY CALCULATED FROM THE UNIQUAC ASSOCIATED-SOLUTION MODEL

In a ternary mixture containing one alcohol and two hydrocarbons, A stands for the alcohol, B for the aromatic hydrocarbon, and C for the saturated hydrocarbon. The association constants of the alcohol are expressed by eqns. (5) and (6).

A solvation equilibrium is assumed between the terminal hydroxyl group of alcohol linear i-mers and one aromatic hydrocarbon

$$A_i + B = A_iB \quad K_{AB} = \frac{\phi_{A_iB_1}}{\phi_{A_i}\phi_{B_1}} \frac{i}{r_{A_iB_1}} \qquad \text{for all } i \geqslant 1 \tag{8}$$

In this work we use a single value of $h_A = -23.2$ kJ mol^{-1}, which is equivalent to the enthalpy of dilution of ethanol in n-hexane at 25°C [11] and is assumed to be independent of the degree of association.

The total enthalpy of complex formation in the mixture is given by

$$H_f = h_A \left[n_{A_2} + \sum_{i=3}^{\infty} (i-1)(n_{A_i} + n_{A_iB_1}) + h_{AB} \sum_{i=1}^{\infty} n_{A_iB_1} \right] \Big/ (n_A + n_B + n_C) \tag{9}$$

and H_f^*, the value of H_f for pure alcohol, is expressed as

$$H_f^* = h_A \left\{ n_{A_2}^* + \sum_{i=3}^{\infty} (i-1) n_{A_i}^* \right\} \Big/ n_A^* \tag{10}$$

Then, the chemical contribution to the excess enthalpy of the mixture is defined by

$$H_{\text{chem}}^E = H_f - x_A H_f^* \tag{11}$$

The final expression of eqn. (11) is derived as

$$\begin{aligned} H_{\text{chem}}^E = {} & h_A x_A \frac{K_2 \phi_{A_1}^2}{\phi_A (1 - K_A \phi_{A_1})^2} \left[1 + K_{AB} r_A \phi_{B_1}\right] \\ & + h_{AB} x_A K_{AB} r_A \frac{\phi_{A_1}\phi_{B_1}}{\phi_A} \left[1 + \frac{K_2 \phi_{A_1}}{(1 - K_A \phi_{A_1})}\right] - h_A x_A \frac{K_2 \phi_{A_1}^{*2}}{(1 - K_A \phi_{A_1}^*)^2} \end{aligned} \tag{12}$$

where ϕ_A is the nominal segment fraction of the alcohol given by eqn. (13)

and the monomer segment fractions, ϕ_{A_1} and ϕ_{B_1} are obtained by numerically solving mass balance equations expressed by eqns. (14) and (15).

$$\phi_I = \frac{r_I x_I}{\sum_J r_J x_J} \tag{13}$$

$$\phi_A = \left[\phi_{A_1} + \frac{K_2 \phi_{A_1}^2 (2 - K_A \phi_{A_1})}{(1 - K_A \phi_{A_1})^2}\right]\left[1 + K_{AB} r_A \phi_{B_1}\right] \tag{14}$$

$$\phi_B = \phi_{B_1}\left\{1 + K_{AB} r_B \phi_{A_1}\left[1 + \frac{K_2 \phi_{A_1}}{(1 - K_A \phi_{A_1})}\right]\right\} \tag{15}$$

The physical contribution is obtained by applying the Gibbs–Helmholtz relation to the residual term of the UNIQUAC equation [1–3].

$$H^E_{\mathrm{phys}} = -R \sum_I q_I x_I \frac{\sum_J \theta_J \frac{\partial \tau_{JI}}{\partial (1/T)}}{\sum_J \theta_J \tau_{JI}} \tag{16}$$

where θ_J is the overall surface fraction given by eqn. (17) and τ_{JI} is related to the energy parameter a_{JI} by eqn. (18).

$$\theta_I = \frac{q_I x_I}{\sum_J q_J x_J} \tag{17}$$

$$\tau_{JI} = \exp[-a_{JI}/T] \tag{18}$$

We assume that a_{JI} has a linear temperature-dependence indicated by

$$a_{JI} = C_I + D_I(T - 273.15) \tag{19}$$

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

$$H^E = H^E_{\mathrm{chem}} + H^E_{\mathrm{phys}} \tag{20}$$

TABLE 3

Solvation equilibrium constants and enthalpies of complex formation

Mixture (A–B)	K_{AB} at 50°C	$-h_{AB}$ (kJ mol^{-1})
Ethanol–benzene	3	8.3
Ethanol–toluene	3	8.3
Ethanol–*p*-xylene	3	8.3
1-Propanol–*p*-xylene	2.5	8.3
2-Propanol–benzene	2.5	8.3
2-Propanol–toluene	2.5	8.3
2-Propanol–*p*-xylene	2.5	8.3

RESULTS

Table 3 lists the solvation constants and the enthalpies for complex formation [12]. Table 4 represents the absolute arithmetical mean deviations

TABLE 4

Calculated results for binary mixtures at 25°C

Mixture (A–B)	No. of data points	Abs. arith. mean dev. (J mol^{-1})	Parameters				Ref.
			C_A (K)	C_B (K)	D_A	D_B	
Ethanol–cyclohexane	20	0.8	−97.60	258.40	−0.5665	0.9085	13
Ethanol–benzene	10	2.3	472.56	450.08	0.9103	1.7702	14
Ethanol–toluene	10	2.6	510.39	681.57	1.3090	2.7198	14
Ethanol–*p*-xylene	16	2.2	580.32	178.18	1.6451	0.6829	3
1-Propanol–cyclohexane	18	4.3	207.43	−150.66	0.2818	−0.4864	13
1-Propanol–*p*-xylene	16	5.0	319.98	67.33	0.4874	−0.1355	3
2-Propanol–cyclohexane	18	3.2	409.65	−180.01	2.2560	−1.0608	15
2-Propanol–methylcyclohexane	19	8.4	505.25	−252.68	2.7674	−1.2038	16
2-Propanol–benzene	10	5.0	32.75	−18.62	−0.0648	−0.4184	14
2-Propanol–toluene	10	3.9	54.47	−22.88	0.1716	−0.4213	14
2-Propanol–*p*-xylene	18	1.7	105.87	−250.24	−0.1684	−0.7938	3
Benzene–cyclohexane	24	1.1	129.03	65.35	0.0963	−0.1206	13
Methylcyclohexane–benzene	17	0.7	79.36	114.45	−0.0344	0.0674	16
Toluene–cyclohexane	12	3.2	86.58	22.96	−0.0806	−0.0021	17
p-Xylene–cyclohexane	19	3.3	29.46	18.07	−0.9439	0.7911	3

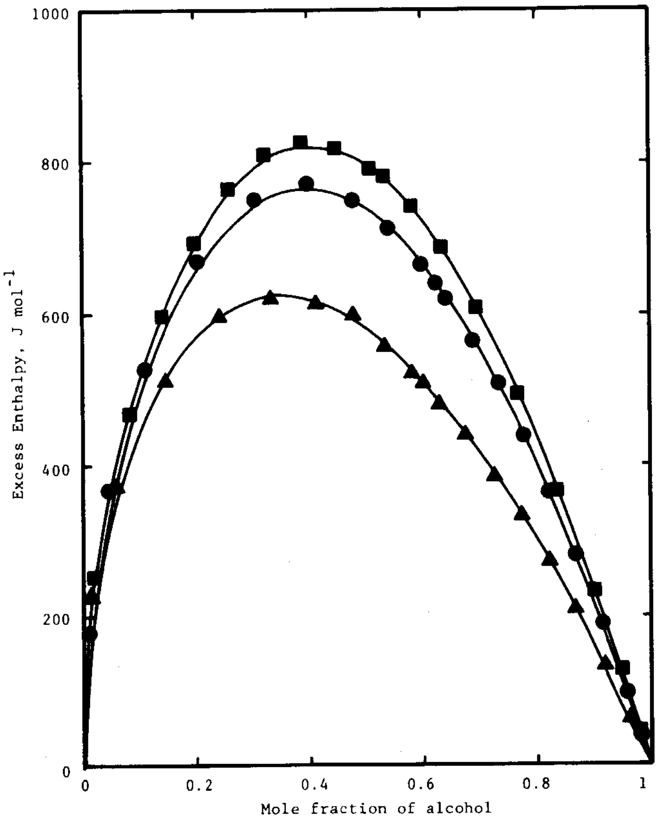
TABLE 5

Predicted results for ternary excess enthalpies at 25°C

Mixture (A–B–C)	No. of data points	Abs. arith. mean dev. (J mol^{-1})		Ref.
		I [a]	II [b]	
Ethanol–benzene–cyclohexane	18	14.5	24.3	18
Ethanol–toluene–cyclohexane	8	14.8	18.1	18
Ethanol–*p*-xylene–cyclohexane	59	9.1	25.8	3
1-Propanol–*p*-xylene–cyclohexane	42	5.1	12.9	3
2-Propanol–benzene–cyclohexane	67	18.1	33.3	15
2-Propanol–benzene–methylcyclohexane	61	13.3	18.4	16
2-Propanol–toluene–cyclohexane	56	10.8	9.8	19
2-Propanol–*p*-xylene–cyclohexane	55	12.1	13.6	3

[a] This work.

[b] Nagata and Ogasawara [3].



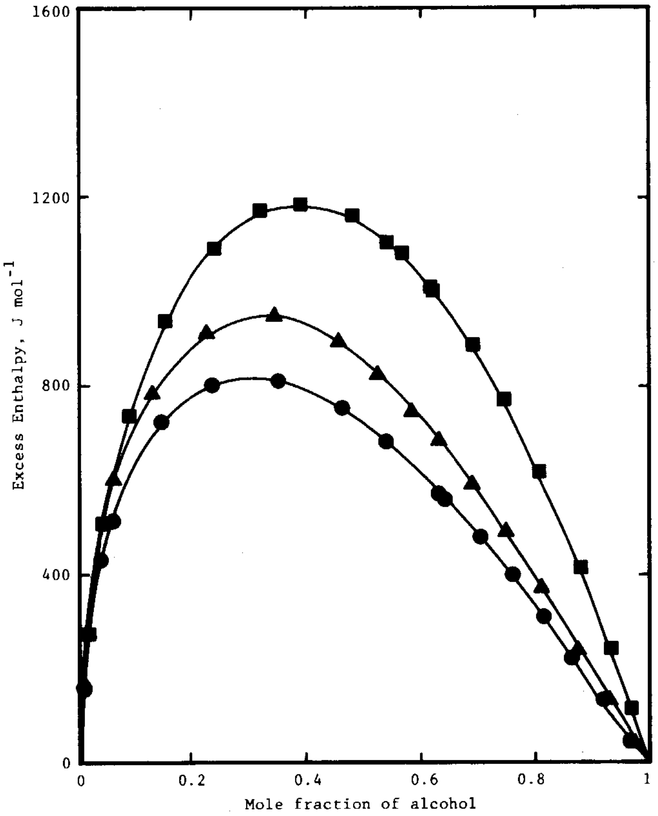


Fig. 1. Comparison of model with experiment for the molar excess enthalpy, H^E, at 25°C of alcohol–saturated hydrocarbon mixtures. Experimental results: (▲) 1-propanol–cyclohexane, data of Nagata and Kazuma [13]; (●) 2-propanol–methylcyclohexane, data of Nagata et al. [16]; (■) 2-propanol–cyclohexane, data of Nagata et al. [15]. Calculated value (———).

Fig. 2. Comparison of model with experiment for the molar excess enthalpy, H^E, at 25°C of alcohol–*p*-xylene mixtures. Experimental results of Nagata and Ogasawara [3]: (●) ethanol–p-xylene; (▲) 1-propanol–*p*-xylene; (■) 2-propanol–*p*-xylene. Calculated value (———).

between experimental and calculated values obtained in fitting the UNIQUAC associated-solution model to binary excess enthalpy results. The calculated H^E curves are compared with the experimental data of the three alcohol–saturated hydrocarbon mixtures in Fig. 1. Figure 2 also shows the results for the three alcohol–*p*-xylene mixtures. Only the binary parameters were used to predict ternary excess enthalpies for mixtures of one alcohol with two hydrocarbons. Table 5 gives the predicted results for eight ternary mixtures. From these results we conclude that the present approach is better than the previous one [3] for predicting the ternary excess enthalpies of alcohol–hydrocarbon mixtures.

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NOTATION

A, B, C	alcohol, aromatic hydrocarbon, and saturation hydrocarbon, respectively
a_{JI}	energy pàrameter
B_A^F	second virial coefficient of homomorph
C_I, D_I	coefficients of eqn. (19)
F	objective function of eqn. (7)
H_f	total enthalpy of complex formation
H^E	excess molar enthalpy
h_2	enthalpy of formation of one mole of hydrogen bond for dimer
h_A	enthalpy of formation of one mole of hydrogen bond for *i*-mer, $i > 2$
h_{AB}	enthalpy of complex formation between alcohol and aromatic hydrocarbon
K_2	association equilibrium constant for dimer
K_A	association equilibrium constant for *i*-mer, $i > 2$
K_{AB}	solvation equilibrium constant between alcohol and aromatic hydrocarbon
n	number of moles of a particular species
P^c	critical pressure
P^s	saturated vapor pressure
q	pure-component molecular surface parameter
r	pure-component molecular size parameter

R	gas constant
T	absolute temperature
T^{b}	normal boiling point
T^{c}	critical temperature
$v_{\mathrm{A}}^{\mathrm{L}}$	liquid molar volume of alcohol
x	liquid-phase mole fraction

Greek letters

γ	activity coefficient
Θ_{h}	parameter for the hypothetical fluid defined as $\Theta_{\mathrm{h}} = T_{\mathrm{h}}^{\mathrm{b}}/T_{\mathrm{h}}^{\mathrm{c}}$
θ	surface fraction
τ_{JI}	$\exp[-a_{JI}/T]$
ϕ	segment fraction

Subscripts

A, B, C	alcohol, aromatic hydrocarbon, and saturated hydrocarbon, respectively
chem	chemical
h	hypothetical fluid (homomorph)
I, J	components
phys	physical

Superscript

*	pure liquid alcohol

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