International Journal of Thermophysics, Vol. 16, No. 5, 1995

An Association Model for Mixtures Containing Any Number of Alkanes and Any Number of Alcohols: Application to Alcohol–Alkane Binary Systems[1]

C. A. Schmidt[2] and S. W. Campbell[2,3]

A previously derived association model for mixtures of any number of alcohols and alkanes is applied here to alcohol–alkane binary systems. The model contains two adjustable parameters: a self-association constant for the alcohol and a parameter that reflects physical interactions. Correlations for the two parameters are presented which allow the model to be used as a two-, one-, or zero-parameter model, depending on the amount of experimental data available. All three forms of the model provide adequate results for these systems over a fairly wide temperature range.

KEY WORDS: alcohols; alkanes; association; hydrogen bonding; vapor–liquid equilibrium.

1. INTRODUCTION

In a previous publication [1], Flory-Huggins theory, regular solution theory, and chemical equilibria were used to develop an association model for mixtures containing any number of alkanes and any number of alcohols. The derivation of the model assumes that the alcohols in the mixture form linear complexes due to hydrogen bonding. The length and composition of each complex are determined from chemical equilibria among the various alcohols present. The alkanes are assumed to be inert species that do not solvate with the alcohol chains.

A simple model containing few adjustable parameters was deliberately chosen so as to allow accurate computation of vapor–liquid equilibria from

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[1] Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19–24, 1994, Boulder, Colorado, U.S.A.

[2] Department of Chemical Engineering, University of South Florida, Tampa, Florida 33620, U.S.A.

[3] To whom correspondence should be addressed.

0195-928X/95/0900-1299$07.50/0

limited or nonexistent data. All parameters in the model can be evaluated from binary data. In the previous work, the model was applied to binary systems of two alcohols, binary systems of an alcohol with an alkane, ternary systems of two alcohols and an alkane, and ternary systems of three alcohols. No attempt was made to develop generalized correlations for any of the model parameters.

In this paper, correlations for the model parameters for binary alcohol–alkane systems are presented.

2. THE ASSOCIATION MODEL

The simple association model, in the form of an expression for the activity coefficient γ_m of a species m in a multicomponent mixture of alcohols and alkanes, is

$$\ln \gamma_m = \ln \left(\frac{C_{m,1}}{x_m C^0_{m,1}} \right) - r_m(\Psi - \Psi_{\text{pure } m}) + \frac{r_m}{RT} \sum_i \sum_j \phi_i \phi_j (\beta_{im} - \beta_{ij}/2) \quad (1)$$

where x_m is the mole fraction of species m, $C_{m,1}$ is the concentration of monomers of species m in the mixture, $C^0_{m,1}$ is the concentration of monomers of species m in pure m, Ψ is the total concentration of all complexes in the mixture, and $\Psi_{\text{pure } m}$ is the concentration of all complexes in pure species m. The quantity β_{ij} is the regular solution parameter and r_m is a size parameter that is defined as the ratio of the saturated liquid molar volume of species m to that of methanol at 303.15 K. The volume fraction ϕ_i of species i is then given by

$$\phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad (2)$$

For a given set of liquid mole fractions in a mixture of k species, the activity coefficient of a species m is found by the following steps. First, the following k equations are solved simultaneously for k values of Ψ_m:

$$\Psi_m = \frac{\phi_m}{r_m(1 + \sum_i K_{im} \Psi_i)}, \qquad m = 1, 2, \ldots, k \quad (3)$$

The total concentration Ψ is then found from

$$\Psi = \sum_m \Psi_m \quad (4)$$

The concentration $C_{m,1}$ of each monomer of species m is obtained from

$$C_{m,1} = \frac{\Psi_m^2 r_m}{\phi_m} \tag{5}$$

The concentration $C_{m,1}^0$ of monomer m in pure m is obtained for each species by solving

$$1/r_m = \frac{C_{m,1}^0}{(1 - K_{mm} C_{m,1}^0)^2} \tag{6}$$

and $\Psi_{\text{pure } m}$ is found for each species m by

$$\Psi_{\text{pure } m} = \frac{C_{m,1}^0}{(1 - K_{mm} C_{m,1}^0)} \tag{7}$$

The quantities $C_{m,1}^0$, $C_{m,1}$, $\Psi_{\text{pure } m}$, and Ψ are substituted into Eq. (1) to obtain the activity coefficient of species m. The quantities K_{ij} are referred to as self-association constants if alcohols i and j are identical and they are called cross-association constants if alcohols i and j are different. For any alkane species i, K_{ii} is zero because alkanes do not self-associate and K_{ij} is zero since they do not associate with other alkanes and it is assumed that they do not solvate with alcohols.

For a binary mixture of an alcohol (A) with an alkane (B), the model contains two adjustable parameters; the alcohol self-association constant K_{AA} and the regular solution parameter β_{AB}. For a binary mixture of alcohol (A) and alcohol (B), it is assumed that the self-association constants K_{AA} and K_{BB} of both alcohols are known from binary alcohol–alkane data. The model then contains two adjustable parameters; the cross-association constant K_{AB} and the regular solution parameter β_{AB}. For mixtures of alkane (A) and alkane (B) the model contains the single adjustable parameter β_{AB}. No additional adjustable parameters are required for multicomponent systems.

To develop a predictive model for systems containing any number of alcohols and any number of alkanes, it is therefore necessary to consider three types of binary subsets: alkane–alkane, alcohol–alkane, and alcohol–alcohol. A correlation of the model parameters for alcohol–alkane binary systems is presented here.

3. ALCOHOL–ALKANE BINARY SYSTEMS

Parameters K_{AA} and β_{AB} have been obtained by regression of vapor–liquid equilibrium data for 45 alcohol–alkane binary systems. Space limitations do not allow a listing of the parameter values and data references but

Table I. Results of Comparison Between Model and Experimental Data for Case I, Case II, and Case III Using the Association Model or the UNIFAC Model for the 148 Binary Alcohol–Alkane Isotherms Studied

Mixtures which contain	No. of isotherms	Temp. range (°C)	Case I		Case II		Case III		UNIFAC	
			% ΔP^a	$\Delta y_1{}^b$	% ΔP^a	$\Delta y_1{}^b$	% ΔP^a	$\Delta y_1{}^b$	% ΔP^a	$\Delta y_1{}^b$
Methanol	12	20–150	1.22	0.0108	1.59	0.0107	1.90	0.0127	4.66	0.0348
Ethanol	20	10–150	0.84	0.0065	1.03	0.0080	3.10	0.0123	3.88	0.0173
Propan-1-ol	17	5–75	0.49	0.0042	0.77	0.0058	2.92	0.0107	3.46	0.0171
Propan-2-ol	13	25–75	0.58	0.0062	1.09	0.0090	3.12	0.0157	3.72	0.0211
Butan-1-ol	10	25–115	0.35	0.0034	0.66	0.0048	0.94	0.0054	3.52	0.0090
Butan-2-ol	3	30–75	0.63	0.0077	0.76	0.0087	1.37	0.0104	4.56	0.0180
2-Methylpropan-1-ol	4	25–65	0.37	0.0038	0.48	0.0047	1.48	0.0086	2.92	0.0098
2-Methylpropan-2-ol	3	40	0.66	0.0050	2.13	0.0151	2.58	0.0170	6.16	0.0253
Pentan-1-ol	11	25–95	0.39	0.0020	0.59	0.0019	1.64	0.0034	3.56	0.0064
Pentan-2-ol	3	75–95	0.32	0.0051	0.50	0.0055	0.60	0.0062	3.50	0.0173
Pentan-3-ol	3	75–95	0.17	0.0032	0.68	0.0040	0.78	0.0052	5.49	0.0261
2-Methylbutan-1-ol	3	75–95	0.33	0.0041	0.51	0.0044	0.59	0.0049	2.11	0.0109
3-Methylbutan-1-ol	3	75–95	0.32	0.0064	0.43	0.0064	0.54	0.0065	1.65	0.0123
2-Methylbutan-2-ol	3	55–75	0.18	0.0061	1.30	0.0098	1.71	0.0120	7.49	0.0350
Hexan-1-ol	14	20–100	0.40	NA[c]	0.64	NA	0.92	NA	6.93	NA
2,3,3-Trimethylbutan-2-ol	8	25–90	1.30	NA	3.67	NA	4.00	NA	8.81	NA
Octan-1-ol	1	40	1.24	NA	1.17	NA	1.13	NA	6.98	NA
Decan-1-ol	7	10–60	0.22	NA	0.39	NA	1.47	NA	11.99	NA
Dodecan-1-ol	10	25–70	0.30	NA	0.48	NA	0.83	NA	13.97	NA
Overall average	148		0.58	0.0051	0.96	0.0067	1.93	0.0098	4.92	0.0175

[a] Average percentage deviations in pressure for all isotherms which contain the same alcohol.

[b] Average deviation in vapor-phase mole fraction for all isotherms which contain the same alcohol.

[c] No vapor-phase mole fraction data available or used.

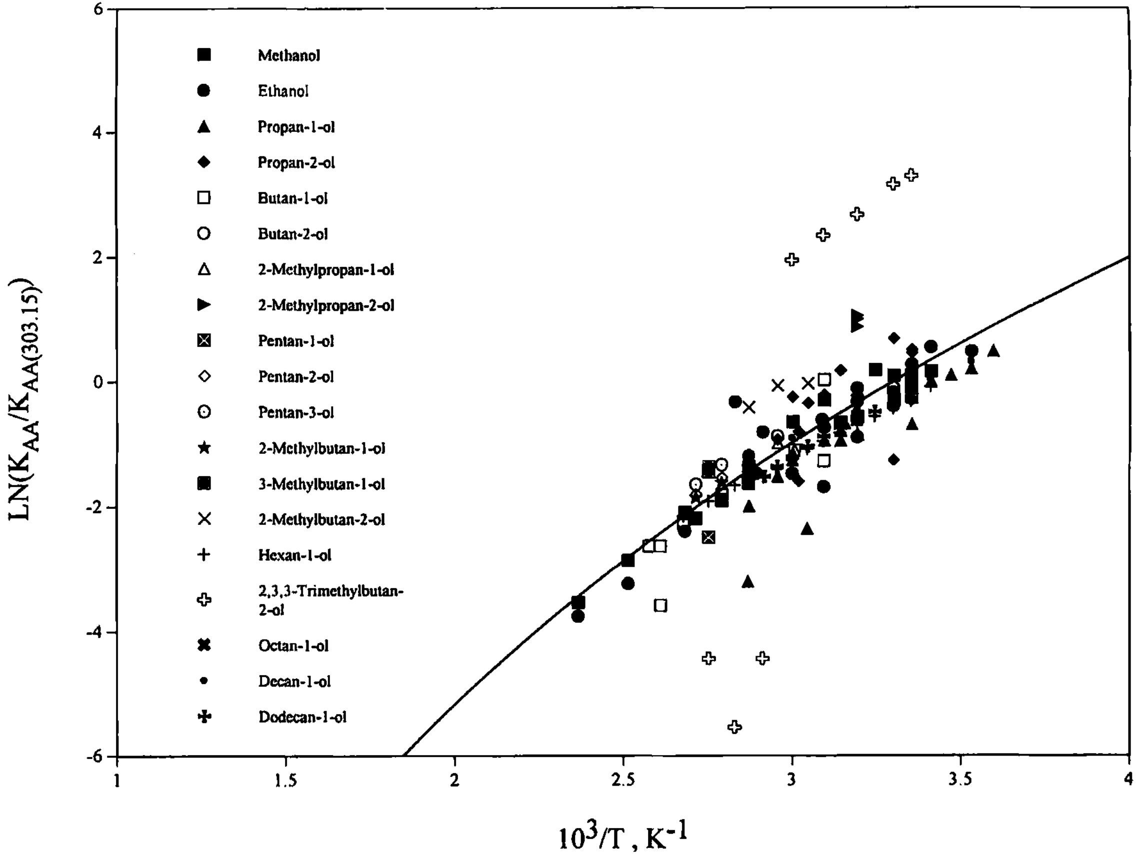

Fig. 1. Relationship between alcohol self-association constant K_{AA} and temperature for various alcohols.

they are available in Ref. 2. The data for 45 systems are comprised of 148 isotherms, with a total of 2217 measured pressures and liquid-phase compositions and 1120 measured vapor-phase compositions. The alkanes range from *n*-butane to *n*-decane and include isooctane and several isomeric hexanes.

Regressions were performed using Barker's method [3], in which the sum of the squares of the differences between calculated and measured pressures is minimized. Resulting average deviations in pressure and (if measured) vapor phase mole fraction are given in Table I under Case I. In all calculations, vapor-phase nonidealities were modeled with the two-term pressure-explicit virial equation, and Poynting factors were included. Second virial coefficients and saturated liquid volumes, when not included with the data, were estimated using the methods of Tsonopoulos [4] and Spencer and Adler [5], respectively.

Following Renon and Prausnitz [6], it was next assumed that the enthalpy of hydrogen bonding was the same for all alcohols. From this, it follows that

$$\ln \frac{K_{AA}(T)}{K_{AA}(T_{ref})} = f(T) \tag{8}$$

where the function $f(T)$ is the same for all alcohols and where the reference temperature is 303.15 K. A regression of the self-association constants obtained in Case I was performed to yield $K_{AA}(T_{ref})$ for each alcohol and parameters that appear in the function $f(T)$. It was found that

$$f(T) = -10.783 \ln \left(\frac{T}{T_{ref}} \right) \tag{9}$$

provided a good representation of the temperature dependence of the self association constants. A comparison of this correlation with the values of K_{AA} obtained from Case I is shown in Fig. 1. Values of the self-association constants at 303.15 K are presented in Table II.

Using this correlation for the self-association constants results in a model that has a single adjustable parameter β_{AB}. The results presented in Table I under Case II show how the association model performs as a one-parameter model. In this case a new value of the parameter β_{AB} was determined for each system since the association constants obtained from Eqs. (8) and (9) are slightly different from their original values.

Next, an attempt was made to relate the parameter β_{AB} to molecular structures of the alcohols and alkanes. It was found that β_{AB} depended strongly on which alcohol was present but was insensitive to the alkane.

Table II. Self-Association Constant K_{AA} at $T_{ref} = 303.15$ K and Effective Carbon Numbers Cne for C_1–C_{12} Alcohols

Alcohol	K_{AA}	Cne
Methanol	365.6	1.00
Ethanol	382.7	2.00
Propan-1-ol	282.9	3.00
Propan-2-ol	77.7	2.30
Butan-1-ol	230.8	4.00
Butan-2-ol	71.0	3.10
2-Methylpropan-1-ol	154.1	3.53
2-Methylpropan-2-ol	18.2	2.26
Pentan-1-ol	204.9	5.00
Pentan-2-ol	86.7	4.06
Pentan-3-ol	58.2	3.88[a]
2-Methylbutan-1-ol	154.2	4.54[a]
3-Methylbutan-1-ol	196.8	4.67[a]
2-Methylbutan-2-ol	24.6	3.23[a]
Hexan-1-ol	234.8	6.00
2,3,3-Trimethylbutan-2-ol	2.6	2.07[a]
Octan-1-ol	153.8	8.00
Decan-1-ol	171.3	10.00
Dodecan-1-ol	216.2	12.00

[a] Effective carbon numbers were calculated using the correlation of Ambrose and Sprake [7].

Furthermore, this parameter was found to be insensitive to temperature. Hence, β_{AB} may be related to some characteristic property of the alcohols. The effective carbon numbers presented by Ambrose and Sprake [7] were selected for this purpose and their values for different alcohols are given in Table II. The parameter β_{AB} for each alcohol (averaged over all isotherms for which that alcohol was a component) is plotted versus effective carbon number Cne of the alcohol in Fig. 2. A good representation of this parameter is provided by

$$\beta_{AB} = 260.71 + 1364.55 e^{-0.6866\mathrm{Cne}} \tag{10}$$

where β_{AB} is in $\mathrm{J \cdot mol^{-1}}$. With the correlation given by Eq. (10), the model for alcohol–alkane binary systems requires no parameter estimation and the results of its application are given in Table I under Case III. For comparison, the results of applying another such method, UNIFAC, are also presented in Table I. The superiority of Case III over UNIFAC is not unexpected since Case III is based on more information obtained from

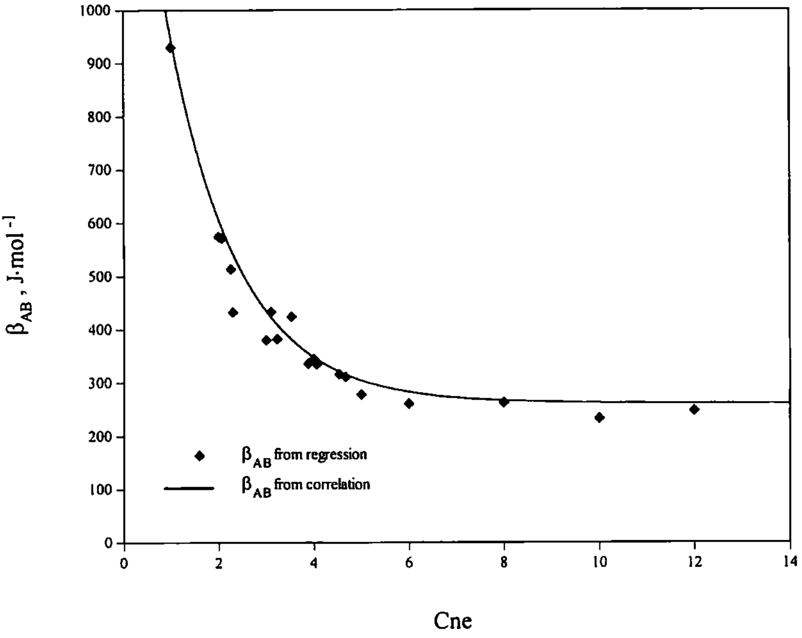

Fig. 2. Relationship between the physical parameter β_{AB} for alcohol–alkane binary systems and the effective carbon number of the alcohol.

experiment than is UNIFAC (a reference self-association constant for each pure alcohol as opposed to two parameters which characterize interactions between CH and OH groups). Furthermore, UNIFAC applies to a wide variety of different systems beyond alkanes and alcohols. Nevertheless, the comparison shown in Table I indicates the promise for predictive thermodynamic models in which association through hydrogen bonding is explicitly accounted for.

4. CONCLUSIONS

A previously derived association model for systems containing any number of alcohols and alkanes was applied to binary alcohol–alkane systems. The number of parameters can be taken to be zero, one, or two, depending on the amount of information available for parameter estimation. Even the fully predictive form provides adequate results.

The application of the model to binary alcohol–alcohol systems is currently under examination.

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Printed in Belgium
Verantwoordelijke uitgever:
Hubert Van Maele
Altenastraat 20 – B-8310 St.-Kruis