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On the Temperature Dependence of ASOG Parameters for VLE Calculations

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A simple and efficient method for generating vapor-liquid equilibrium (VLE) values for mixtures where data are lacking is always in demand because VLE data are essential in distillation design calculations. One of the frequently used methods is the analytical-solution-of-groups (ASOG) method. All molecules are considered to be consisting of a number of functional groups. The nonideal behavior of a component in a mixture, expressed in terms of activity coefficient, is due to the differences in molecular size (configurational contribution) and in intermolecular forces originating from the different functional groups (group-interaction contribution). Therefore, the ASOG method involves the reduction of activity coefficients, obtained from experimentally determined VLE values, into a number of binary group interaction parameters. Successful application of these parameters in the prediction of VLE values at various isobaric/isothermal conditions requires that their temperature dependence be properly represented. Otherwise, poor results are obtained.

The logarithm of the activity coefficient of component i in a mixture is expressed by the sum of $\ln\gamma_i^S$, the size contribution which depends on the number of size groups in the molecules of the mixture, and $\ln\gamma_i^G$, the contribution due to the interaction of the functional groups of the molecule with those in the mixture. Furthermore, the size term is treated by means of the Flory-Huggins theory for athermal mixtures of unequal-sized molecules. Hence

$$\ln\gamma_i = \ln\gamma_i^S + \ln\gamma_i^G \tag{1}$$

and

$$\ln\gamma_i^S = 1 - \frac{\nu_i}{\sum\limits_j \nu_j x_j} + \ln\frac{\nu_i}{\sum\limits_j \nu_j x_j} \tag{2}$$

In Eq. 2, ν_j and x_j refer to the number of non-hydrogen atoms in molecule j and the liquid mole fraction of component j, respectively. The summation, $\sum\limits_j$, extends over all components, including component i. In addition,

$$\ln\gamma_i^G = \sum_k \nu_{ki}(\ln\Gamma_k - \ln\Gamma_k^{(i)}) \tag{3}$$

where ν_{ki} is the total number of non-hydrogen atoms in all the functional groups of kind k in a molecule of component i, and Γ_k and $\Gamma_k^{(i)}$ are the activity coefficients of the group k in the mixture and in the standard state (pure component i), respectively. The summation, $\sum\limits_k$, extends over all functional groups of the mixture. The quantity, Γ_k, is given by the Wilson equation

$$\ln\Gamma_k = -\ln\sum_l \chi_l a_{kl} + 1 - \sum_l \frac{\chi_l a_{lk}}{\sum\limits_m x_m a_{lm}} \tag{4}$$

where a_{kl} and a_{lk} are the group-interaction parameters, characteristic of the groups k and l, but $a_{kl} \neq a_{lk}$. The summations, $\sum\limits_l$ and $\sum\limits_m$, extend over all the functional groups. The group fraction of group l, χ_l, is given by

$$\chi_l = \frac{\sum\limits_j x_j \nu_{lj}}{\sum\limits_j x_j \sum\limits_k \nu_{kj}} \tag{5}$$

The parameters a_{kl} and a_{lk} are obtained from VLE values and are temperature dependent.

Derr and Deal (1969) plotted the logarithm of the parameters a_{kl} and a_{lk} versus temperature to indicate their temperature dependence and suggested that although these parameters "tend to vary quite regularly with temperature it is hazardous to extrapolate them over large temperature ranges." To illustrate

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Table 1 Group-interaction parameters $b_{\ell\kappa}$ and $b_{\kappa\ell}$, K

(Temperature range: 303.15 to 423.15 K)

κ \ ℓ	CH_2	C=C	A_rCH	C_yCH	H_2O	OH	CO	COO	CN	CCL_3	CCL_4
CH_2	0	4161.7	132.1	2.5	399.8	1452.6	199.7	381.8	237.6	481.2	563.2
C=C	-450.0	0	-79.5	*	*	-7.9	-74.9	629.7	7.5	65.4	92.2
A_rCH	-88.8	317.0	0	45.7	*	357.9	156.1	522.0	120.0	509.0	553.0
C_yCH	-2.0	*	-21.4	0	*	10705.	211.5	*	*	370.0	*
H_2O	1114.9	•	*	*	0	-338.3	231.7	493.1	*	*	*
OH	1421.5	1458.7	1030.9	1267.8	810.3	0	477.9	850.5	816.1	1443.8	1741.7
CO	231.4	486.6	39.1	185.4	102.5	-138.3	0	416.0	26.4	407.3	227.4
COO	-118.4	-139.3	-337.9	•	62.4	-309.0	-283.0	0	*	322.5	168.2
CN	367.1	515.3	197.4	•	*	-166.1	-38.5	•	0	*	829.7
CCL_3	-446.0	279.5	-516.9	-333.2	*	-312.0	-388.6	-284.2	*	0	92.9
CCL_4	-552.7	14468.	-545.3	*	*	137.2	8822.9	7.1	-354.3	-78.2	0

*data are inadequate or totally absent. A_rCH = aromatic carbon C_yCH = cycloalkane

this point they predicted activity coefficients for the components of the nearly ideal binary system xylene-di-isobutyl ketone at 423.15°K using extrapolated parameter values and obtained activity coefficients substantially less than unity. On the other hand, Tochigi and Kojima (1976) suggested that the logarithm of these parameters can be represented as a linear function of $1/T$,

$$\ln a_{kl} = m_{kl} + n_{kl}/T \qquad (6)$$

The quantities, m_{kl} and n_{kl}, are constants and independent of temperature. The object of this study is to modify Eq. 6 with the aim of obtaining a simple but adequate expression for representing the temperature dependence of these parameters.

The proposed equation involves an exponential term of $1/T$ and a ratio of the pair sizes,

$$a_{kl} = (\nu_l/\nu_k)\exp(-b_{kl}/T) \qquad (7)$$

In other words, the quantity m_{kl} of Eq. 6 has been replaced in Eq. 7 by the ratio of the number of non-hydrogen atoms in groups l and k while the quantity n_{kl} has been replaced by $(-b_{kl})$. A similar expression can be used for a_{lk} by interchanging the two subscripts. The numerical values of m_{kl} and n_{kl}, are of course, not necessarily identical to that of $\ln(\nu_l/\nu_k)$ and $(-b_{kl})$ respectively. Equation 7 is very similar to that used for representing the temperature dependence of the Wilson parameters. This simple modification permits the extrapolation of these parameters even from values obtained at a single temperature. Furthermore, it does not require any properties not already used in the calculation procedure of the ASOG method.

In this work, the temperature independent values of b_{kl} and b_{lk}, have been systematically established from experimentally determined VLE values reported in the literature for 86 binary systems at a total of 149 isothermal/isobaric conditions in the temperature range of 303.15 to 423.15°K. These functional groups are useful for predicting VLE values for binary and multicomponent mixtures consisting of paraffins, olefins, aromatics, cycloparaffins, alcohols, water, ketones, esters, nitriles, chloroform and other trichlorides, and carbon tetrachloride.

The VLE values used for determining b_{kl} and b_{lk} values are identical to those used by Kojima and Tochigi (1979) for obtaining the values of m_{kl}, m_{lk}, n_{kl} and n_{lk}, so that the predicted VLE values obtained from Eq. 7 can be meaningfully compared with those obtained from Eq. 6. Furthermore, the same objective function,

$$F_{\text{obj}} = \sum_{j=i}^{S} \sum_{i=1}^{N} (\ln\gamma_i^G,\ \text{expt.} - \ln\gamma_i^G,\ \text{calcd})_j^2 \qquad (8)$$

was used to obtain the optimum values of these parameters. In Eq. 8, N and S are the number of components and the number of data points used in the calculation, respectively. The values of b_{kl} and b_{lk} obtained in this study are reported in Table 1. In addition, thus established values for $b_{CH_2/OH}$, b_{OH/CH_2}, $b_{CH_2/ArCH}$ and b_{ArCH/CH_2} were compared with the corresponding values obtained from isothermal and isobaric data, which were not restricted to the conditions used for obtaining the parameter values reported in Table 1. The comparison is depicted in Figure 1. In this figure, each circle represents the optimum value obtained from a set of isothermal data, while a dotted line represents the optimum value obtained from a set of isobaric data over the indicated temperature range.

In the evaluation of ν_{ki}, CH_3 was considered to be equivalent to CH_2; the values of CH and C in alkanes were taken to be 0.8 and 0.5, respectively, and the value for H_2O was taken to be 1.6. These suggestions were proposed previously by Kojima and Tochigi (1979).

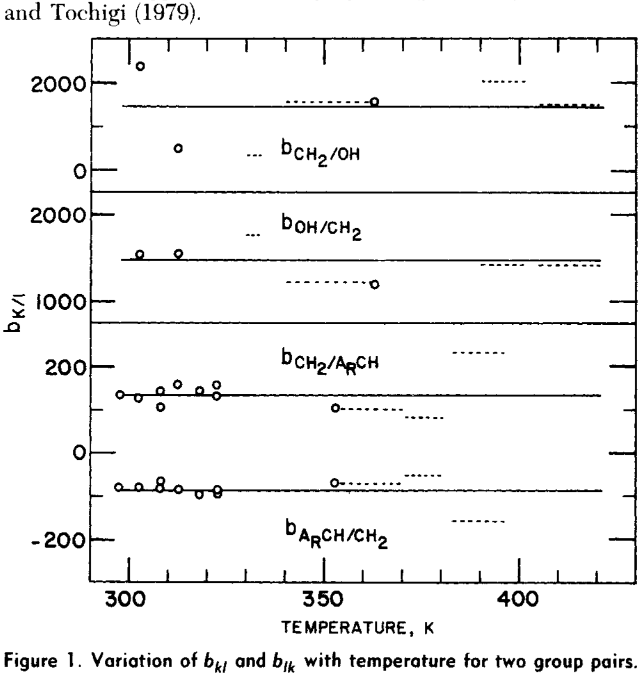

Figure 1. Variation of b_{kl} and b_{lk} with temperature for two group pairs.

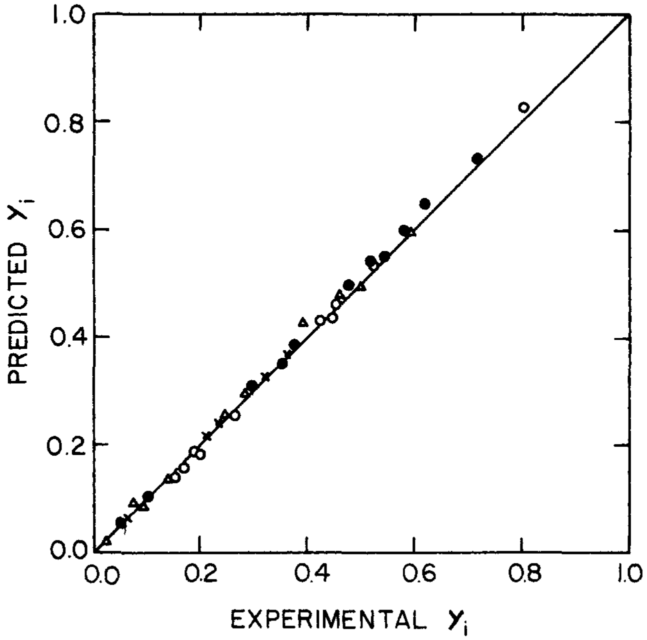

Figure 2. Comparison of calculated and experimental vapor phase compositions for the quaternary system methyl acetate (○)—chloroform (△)—methanol (●)—benzene (×) at 101.325 kN/m². Experimental data were reported by Hudson and Van Winkle (1969).

The parameter values reported in Table 1 were used to generate VLE values for one quinary, three quaternary, 54 ternary and 207 binary systems (including the binaries used for establishing the parameters) for a total of 677 isothermal/isobaric sets of data in the temperature range of 298.15 to 454.15°K. For simplicity, the vapor phase was assumed to be ideal in all the calculations. The calculated values are in reasonably good agreement with the experimental values reported in the literature with an average absolute deviation of 0.013 mol fraction in the vapor phase concentration, indicating that the proposed equation for representing the temperature dependence of these parameters is acceptable. To illustrate the agreement, the calculated vapor phase compositions for the quaternary system methyl acetate-chloroform-methanol-benzene at 101.325 kN/m² are compared with the experimental values reported by Hudson and Van Winkle (1969) in Figure 2. In addition, the calculated γ values for the xylene-di-isobutyl ketone system at 423.15°K are very close to unity, providing another evidence which supports the validity of the proposed equation.

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NOTATION

a_{kl} = temperature-dependent group interaction parameter, Eq. 4
b_{kl} = temperature-independent group interaction parameter, Eq. 7
m_{kl} = temperature-independent group interaction parameter, Eq. 6
n_{kl} = temperature-independent group interaction parameter, Eq. 6
N = number of components
s = number of data points
x = liquid phase mole fraction
y = vapor phase mole fraction

Greek Letters

γ_i = activity coefficient of component i
Γ_k = activity coefficient of group k
ν_i = number of non-hydrogen atoms in molecule i
ν_k = number of non-hydrogen atoms in group k
ν_{ki} = total number of non-hydrogen atoms in all groups of kind k in a molecule of component i
χ = liquid phase group fraction

Subscripts

i, j = component i and j
k, l, m = group k, l, and m
ki = group k in molecule i

Superscripts

G = contribution due to the interaction of the functional groups
(i) = standard state (pure component i)
s = size contribution

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Catalyst Decay by a Leaching Mechanism

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A number of heterogeneous catalysts decay through the loss of a particular specie that is leached or vaporized from the catalyst. Kavasmaneck and Sherman (1980) reported on the advantage of using a recycle reactor to accelerate the decay of catalyst activity for hydration of olefins. Millidge (1969) had previously shown that the activity of a supported phosphoric acid catalyst is dependent on the retention of acid on the support. A theoretical frame work for correlating the catalyst

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