

# DEVELOPMENT AND USE OF A THREE-SUFFIX SCATCHARD—HAMER EQUATION FOR QUATERNARY SYSTEMS

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## Introduction

The vapour-liquid equilibrium of multicomponent non-ideal systems is scantily treated in the literature. This fact can be understood because, in case of a system containing more than three components, the analytical work connected with the equilibrium measurements becomes more difficult, and thus experimental work encounters serious difficulties.

In case of multicomponent systems, the distillation computations are performed for key components [1, 2, 3]; the investigations that can still be performed with satisfactory accuracy are confined to systems containing at the maximum four components. Namely, in this case, starting from some exactly performed measurements, it is possible to determine the activity coefficients characterizing the non-ideal behaviour of the system, and thus to determine the composition of the vapour which is in equilibrium with the liquid phase in the quaternary system, without circuitous work, in theoretical way.

The investigations described in the literature and relating to quaternary systems usually employ the two- and three-suffix MARGULES equations, respectively, developed by WOHL [4] for treating the experimental results [5, 6, 7, 8]. The three-suffix MARGULES equation was supplemented by MAREK, and to increase the correctness of the computation results, he also deduced the four-suffix MARGULES equations [9]. The four-suffix equations contain 18 binary and 12 ternary constants and one quaternary constant, and their applicability is limited by very lengthy computations.

In case of ternary systems, the three- and four-suffix MARGULES equations were successfully employed [10, 11] but our computations performed with the three-suffix quaternary MARGULES equation proved that this equation is not always suitable for correlation of the experimental data, due to lack of correctness [6, 7, 8].

Prompted by the above-mentioned points of view, the development of a quaternary equation was set as an aim which can relatively easily be handled and yet yields a satisfactory correctness.

The extension of the VAN LAAR equations, currently used in case of binary and ternary systems, to quaternary systems did not seem advisable because these equations are not generally valid and their validity is determined by the nature of the corresponding sub-systems [12, 13].

### Theoretical

On the basis of the above considerations, the development of the three-suffix SCATCHARD—HAMER type equations for quaternary systems was decided. As is well-known, the SCATCHARD—HAMER type equations can be developed from the general WOHL equation by substituting volume fractions for the quotient of the effective molal volumes, that is, for the so-called  $q$  fractions. In this way, for describing the anomalous phenomena due to mixing, further characteristics can be introduced in the equations without increasing the number of constants to be experimentally determined.

On deriving the equations, the definition of the SCATCHARD excess free enthalpy of mixing non-ideal systems was taken as a starting point. According to this definition, in a quaternary system composed of components  $i, j, k$  and  $l$ , considering the interaction of three adjoining molecules :

$$\frac{\Delta G^E}{2,303 RT \sum_i^l q_i x_i} = \sum_{ij} z_i z_j a_{ij} + \sum_{ijk} z_i z_j z_k a_{ijk} \quad (1)$$

From this equation, under isothermal and isobar conditions, the activity coefficient of component  $i$  can be calculated on basis of the following equation:

$$\log \gamma_i = \frac{\partial \left[ \sum_i^l n_i \frac{\Delta G^E}{2,303 RT} \right]}{\partial n_i} \quad (2)$$

Accomplishing the operations indicated by eq. (1), after the development and performing the necessary reductions, the following equation is obtained :

$$\begin{aligned} \frac{\Delta G^E}{2,303 RT \sum_i^l q_i x_i} = & 2z_i z_j a_{ij} + 2z_i z_k a_{ik} + 2z_i z_l a_{il} + 2z_j z_k a_{jk} + \\ & + 2z_j z_l a_{jl} + 2z_k z_l a_{kl} + 3z_i^2 z_j a_{iij} + 3z_i z_j^2 a_{iij} + \\ & + 3z_i^2 z_k a_{iik} + 3z_i z_k^2 a_{iik} + 3z_i^2 z_l a_{iil} + 3z_i z_l^2 a_{iil} + \\ & + 3z_j^2 z_k a_{jjk} + 3z_j z_k^2 a_{jjk} + 3z_j^2 z_l a_{jll} + 3z_j z_l^2 a_{jll} + \\ & + 3z_k^2 z_l a_{kll} + 3z_k z_l^2 a_{kll} + 6z_i z_j z_k a_{ijk} + 6z_i z_j z_l a_{ijl} + \\ & + 6z_i z_k z_l a_{ikl} + 6z_j z_k z_l a_{jkl} \end{aligned} \quad (3)$$

The right side is to be multiplied by the coefficient  $2,303 \sum_i^l q_i x_i$  and the following symbols are to be introduced :

$$\begin{aligned}
 A_{ij} &= 2,303 (q_j^2/q_i) [2a_{ij} + 3a_{ijj}] \\
 A_{ji} &= 2,303 q_j [2a_{ij} + 3a_{ijj}] \\
 A_{ik} &= 2,303 (q_k^2/q_i) [2a_{ik} + 3a_{ikk}] \\
 A_{ki} &= 2,303 q_k [2a_{ik} + 3a_{ikk}] \\
 A_{il} &= 2,303 (q_l^2/q_i) [2a_{il} + 3a_{ill}] \\
 A_{li} &= 2,303 q_l [2a_{il} + 3a_{ill}] \\
 A_{jk} &= 2,303 (q_k/q_i)^2 q_j [2a_{jk} + 3a_{jkk}] \\
 A_{kj} &= 2,303 (q_j/q_i)^2 q_k [2a_{jk} + 3a_{jkk}] \\
 A_{jl} &= 2,303 (q_l/q_i)^2 q_j [2a_{jl} + 3a_{jll}] \\
 A_{lj} &= 2,303 (q_j/q_i)^2 q_l [2a_{jl} + 3a_{jll}] \\
 A_{kl} &= 2,303 (q_l/q_i)^2 q_k [2a_{kl} + 3a_{kll}] \\
 A_{lk} &= 2,303 (q_k/q_i)^2 q_l [2a_{kl} + 3a_{kll}] \\
 C_{ijk} &= 2,303 (q_j/q_i) q_k [6a_{ijk} + 2(a_{ij} + a_{ik} + a_{jk})] \\
 C_{ikl} &= 2,303 (q_k/q_i) q_l [6a_{ikl} + 2(a_{ik} + a_{il} + a_{kl})] \\
 C_{ijl} &= 2,303 (q_j/q_i) q_l [6a_{ijl} + 2(a_{ij} + a_{il} + a_{jl})] \\
 C_{jkl} &= 2,303 (q_j/q_i) (q_k/q_i) q_l [6a_{jk} + 2(a_{jk} + a_{jl} + a_{kl})]
 \end{aligned} \tag{4}$$

After reducing and turning to common molar fractions, the following expression is obtained :

$$\begin{aligned}
 \frac{\Delta G^E}{RT} &= \frac{1}{[x_i + (q_j/q_i) x_j + (q_k/q_i) x_k + (q_l/q_i) x_l]^2} [x_i^2 x_j A_{ji} + \\
 &+ x_i x_j^2 A_{ij} + x_i^2 x_k A_{ki} + x_i x_k^2 A_{ik} + x_i^2 x_l A_{li} + x_i x_l^2 A_{il} + \\
 &+ x_j^2 x_k A_{kj} + x_j x_k^2 A_{jk} + x_j^2 x_l A_{lj} + x_j x_l^2 A_{jl} + x_k^2 x_l A_{lk} + \\
 &+ x_k x_l^2 A_{kl} + x_i x_j x_k C_{ijk} + x_i x_j x_l C_{ijl} + \\
 &+ x_i x_k x_l C_{ikl} + x_j x_k x_l C_{jkl}]
 \end{aligned} \tag{5}$$

If, instead of the mole fractions, mole numbers are used, eq. (6) is arrived at:

$$\frac{\Delta \bar{G}^E}{RT} = \frac{1}{n_i + (q_j/q_i) n_j + (q_k/q_i) n_k + (q_l/q_i) n_l^2} [n_i^2 n_j A_{ji} + n_i n_j^2 A_{ij} + n_i^2 n_k A_{ki} + n_i n_k^2 A_{ik} + n_i^2 n_l A_{li} + n_i n_l^2 A_{il} + n_j^2 n_k A_{kj} + n_j n_k^2 A_{jk} + n_j^2 n_l A_{lj} + n_k^2 n_l A_{lk} + n_k n_l^2 A_{kl} + n_i n_j n_k C_{ijk} + n_i n_j n_l C_{ijl} + n_i n_k n_l C_{ikl} + n_j n_k n_l C_{jkl}] \quad (6)$$

According to eq. (2), from this relationship the activity coefficient of the individual components can be obtained by partially deriving eq. (6) with respect to the corresponding mole numbers.

After deriving and performing the possible reductions, and returning to the  $z$  expressions, as well as after replacing the quotient  $q_m/q_n$  by  $V_m/V_n$ , the logarithm of the activity coefficient of component  $i$  (component 1) is given by the following equation :

$$\begin{aligned} \log \gamma_i = & 2z_i z_j (1-z_i) (V_1/V_i) (V_1/V_j) A_{ji} + z_j^2 (1-2z_i) (V_1/V_j)^2 A_{ij} + \\ & + 2z_i z_k (1-z_i) (V_1/V_i) (V_1/V_k) A_{ki} + z_k^2 (1-2z_i) (V_1/V_k)^2 A_{ik} + \\ & + 2z_i z_l (1-z_i) (V_1/V_i) (V_1/V_l) A_{li} + z_l^2 (1-2z_i) (V_1/V_l)^2 A_{il} - \\ & - 2z_j z_k (V_i/V_j) (V_1/V_k) [z_k (V_1/V_k) A_{jk} + z_j (V_1/V_j) A_{kj}] - \\ & - 2z_j z_l (V_i/V_j) (V_1/V_l) [z_l (V_1/V_l) A_{jl} + z_j (V_1/V_j) A_{ij}] - \\ & - 2z_k z_l (V_i/V_k) (V_1/V_l) [z_k (V_1/V_k) A_{lk} + z_l (V_1/V_l) A_{kl}] + \\ & + z_j z_k (1-2z_i) (V_1/V_j) (V_1/V_k) C_{ijk} + z_k z_l (1-2z_i) (V_1/V_k) (V_1/V_l) C_{ikl} + \\ & + z_j z_l (1-2z_i) (V_1/V_j) (V_1/V_l) C_{ijl} - 2z_j z_k z_l (V_i/V_j) (V_1/V_k) (V_1/V_l) C_{jkl} \end{aligned} \quad (7)$$

The activity coefficients relating to components  $j$ ,  $k$  and  $l$  (components 2, 3 and 4) can analogically be obtained by deriving with respect to the mole numbers of the corresponding components or by cyclic permutation. As a matter of course, in the permutation only the factors having suffixes  $i$ ,  $j$ ,  $k$  and  $l$  take part, those having the suffix 1 do not.

From equation (7), the equations relating to the ternary system composed of components  $i$ ,  $j$  and  $k$  (1, 2 and 3) are obtained by omitting the members concerned with the component  $l$  (component 4). Thus, for a ternary system the following equation is obtained :

$$\begin{aligned} \log \gamma_i = & 2z_i z_j (1-z_i) (V_1/V_i) (V_1/V_j) A_{ji} + z_j^2 (1-2z_i) (V_1/V_j)^2 A_{ij} + \\ & + 2z_i z_k (1-z_i) (V_1/V_i) (V_1/V_k) A_{ki} + z_k^2 (1-2z_i) (V_1/V_k)^2 A_{ik} - \\ & - 2z_j z_k (V_i/V_j) (V_1/V_k) [z_k (V_1/V_k) A_{jk} + z_j (V_1/V_j) A_{kj}] + \\ & + z_j z_k (1-2z_i) (V_1/V_j) (V_1/V_k) C_{ijk} \end{aligned} \quad (8)$$

For a binary system, the equations are obtained by omitting the members relating to components  $k$  and  $l$  :

$$\log \gamma_i = 2z_i z_j^2 (V_1/V_i) (V_1/V_j) A_{ji} + (z_i^3 - z_i z_j^2) (V_1/V_j)^2 A_{ij} \quad (9a)$$

$$\log \gamma_j = 2z_i^2 z_j (V_1/V_i) (V_1/V_j) A_{ij} + (z_i^3 - z_i^2 z_j) (V_1/V_i)^2 A_{ji} \quad (9b)$$

It can be seen that at the limiting value  $x_i = 0$  the value of  $\log \gamma_i$  is not identical with the value of the constant  $A_{ij}$ , as in the case of the VAN LAAR or MARGULES equations, but similarly to the SCATCHARD-HAMER equations known from the literature, the limiting value must be corrected with the quotient of the volume fractions.

As can be seen in equations (8) and (9), the relations derived for the binary and ternary systems are not fully identical with the SCATCHARD-HAMER equations described in the literature [14]. This conclusion can be drawn from the fact that when developing the quaternary equations, on choosing the constants, the points of view of manageability of the quaternary system were primarily taken into consideration.

Starting from binary and ternary equilibrium data, the deduced equations ensure the possibility for determining the vapour-liquid equilibrium of quaternary systems with due accuracy.

### Application of the developed equation

In order to demonstrate the use of the developed quaternary equation computations were performed starting from the experimental data presented by DRICKAMER *et al.* [3] on the system isooctane-methylcyclohexane-toluene-phenol.

First of all the constants of the corresponding binary sub-systems have been determined ; the results of these computations are summarized in Table I.

Table I

$A_{ij}$	0,300	$A_{ji}$	0,585
$A_{ik}$	0,053	$A_{ki}$	0,060
$A_{il}$	0,066	$A_{li}$	0,247
$A_{jk}$	-0,250	$A_{kj}$	0,694
$A_{jl}$	0,423	$A_{lj}$	0,263
$A_{kl}$	0,288	$A_{lk}$	0,300

The binary constants of the developed modified SCATCHARD-HAMER equation were determined from the equilibrium data to be found in the literature [3, 15, 16]. It has to be mentioned that the experimental data on the

system methylcyclohexane—toluene seem to be unreliable to a certain extent, recognizable from the different signs of the constants  $A_{jk}$  and  $A_{kj}$ .

The computations carried out on the corresponding binary systems with the aid of the constants listed above gave satisfactory results.

In the interest to get the ternary constants data of only two ternary systems were to be found, namely those of the systems isooctane—toluene—phenol and methylcyclohexane—toluene—phenol, respectively [3]. Constants for the systems isooctane—methylcyclohexane—toluene and isooctane—methylcyclohexane—phenol were computed starting from the quaternary equilibrium isooctane—methylcyclohexane—toluene—phenol, with the aid of the new quaternary equation.

The ternary constants used in the further calculations are summarized in Table II.

Table II

$C_{ijk}$	— 0,77	$C_{ikl}$	+ 2,92
$C_{jki}$	+ 8,10	$C_{kli}$	— 2,90
$C_{kil}$	+ 20,52	$C_{lik}$	— 14,28
$C_{ijl}$	+ 1,84	$C_{jkl}$	+ 1,28
$C_{jli}$	— 7,74	$C_{kij}$	— 4,52
$C_{lij}$	— 2,62	$C_{ljk}$	+ 3,67

It is worth mentioning that the values of the individual ternary constants depend on the ternary equation used for the computations, i. e.

$$C_{ijk} \neq C_{jki} \neq C_{kij} \quad (10)$$

depending on the fact whether the equation for  $\log \gamma_i$ ,  $\log \gamma_j$  or  $\log \gamma_k$  has been used, respectively.

Based on the values of the corresponding binary and ternary constants computations were performed on the quaternary system isooctane—methylcyclohexane—toluene—phenol.

The results obtained compared with the experimental data of DRICKAMER *et al.* [3] are presented in Table III.

Table III

Temp.	$x_1$	$x_2$	$x_3$	$x_4$	$Y_1$		$Y_2$		$Y_3$		$Y_4$	
					exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.
110,0	0,204	0,177	0,182	0,437	0,437	0,370	0,313	0,191	0,184	0,416	0,066	0,023
111,7	0,121	0,238	0,137	0,504	0,304	0,307	0,489	0,494	0,150	0,152	0,057	0,047
112,8	0,135	0,127	0,224	0,514	0,390	0,394	0,284	0,287	0,262	0,264	0,064	0,055
115,5	0,080	0,263	0,189	0,468	0,188	0,210	0,526	0,615	0,212	0,114	0,074	0,061
117,2	0,089	0,078	0,176	0,657	0,406	0,469	0,249	0,188	0,264	0,211	0,081	0,132

The agreement in some cases is quite satisfactory; the deviations in certain points are probably due to analytical inaccuracies which might be demonstrated by the scattering of the values of the activity coefficients in the quaternary data determined experimentally.

### Summary

Starting from the SCATCHARD-type equation giving definition for the excess free enthalpy, a three-suffix SCATCHARD-HAMER type equation for quaternary systems was deduced which, by using the constants of the binary and ternary systems described below, makes possible the direct computation of the vapour-liquid equilibrium of non-ideal quaternary systems. The applicability of the developed equation was shown on the system isooctane-methylcyclohexane-toluene-phenol.

### Symbols used

$A_{ij}$ and $A_{ji}$ , resp.	= constants of the SCATCHARD-HAMER equation of the binary system
$C_{ijk}$	= constant of the SCATCHARD-HAMER equation of the ternary system
$\Delta G^E$	= excess free enthalpy of mixing per mole
$\Delta G_i^E$	= excess free enthalpy of mixing
$V_i$	= actual molecular volume of component $i$
$R$	= universal gas constant
$T$	= equilibrium temperature
$a_{ij}$ and $a_{ijk}$ , resp.	= constants of the equations considering the interaction occurring when mixing the components $i$ and $j$ , and $i$ , $j$ and $k$ , resp.
$q_i$	= effective molal volume of component $i$
$x_i$	= molar fraction of component $i$ in the liquid phase
$z_i$	= effective volume fraction of component $i$
$\gamma_i$	= activity coefficient of component $i$

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