CONDITIONS FOR EXECUTING COMPUTATIONS ON BINARY VAPOUR–LIQUID EQUILIBRIA

By

J. HOLLÓ, T. LENGYEL and A. MÉSZÁROS

Department of Agricultural Chemical Technology, Polytechnical University, Budapest

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Introduction

When executing computations on vapour—liquid equilibria, some equilibrium data, generally considered to be reliable, are taken as the basis for starting point. The correctness of the generally used equations is determined by the reliability of the constants determined on the basis of these data; therefore, it is extremely important to decide the fact as to whether the available values may be used as a basis for further computations. To solve this problem is not a simple task even if more equilibrium data are available. During our investigations, the ranges of validity of a three-suffix Margules-type, a Scatchard—Hamer-type and a modified Scatchard—Hamer-type equation and especially the relation of the constants of the equations have been investigated.

Theoretical

The equations mentioned above can be used for describing the relation between the logarithms of the activity coefficients and the compositions of the liquid phase. Each equation gives one solution of the Gibbs—Duhem equation; consequently, it is obvious that the individual activity coefficients are thermodynamically consistent by related to each other and the trends of the $\log \gamma = f(x)$ curves computed with their aid are correct [1].

The absolute values of the activity coefficients of the individual components depend on the correctness of the vapour—liquid equilibrium data used as starting points; therefore, it is practical to limit the values of the constants and their relation to each other, respectively, to be obtained with preliminary computations. This can simply be made by calculating the extreme value of the curve $\log \gamma = f(x)$.

From the type of interaction between the molecules of the components it can be inferred that if in a given binary system the individual components do not behave ideally, but form a regular Hildebrandian mixture, that is, they do not associate and do not form a complex molecule, respectively, then the values of the activity coefficients serving to describe this deviation are higher or lower than unity in case of both components and they converge, respectively, to unity with increase of the concentration of the corresponding component.

According to the Gibbs—Duhem equation, in case of a given binary composition, the slopes of the curves are of opposite sense; therefore, it is obvious that local maximum or minimum cannot be found on any of the curves because otherwise the above-mentioned conditions could not be fulfilled. Only one generally-cited exception from this statement is known, namely the system chloroform—ethanol [2], but obviously in this case a complex is formed [3], moreover the arising maximum is very low.

The facts mentioned above mean that in the concentration range $0 < x < 1$ being physically interpretable, the curves cannot have an extreme value, that is the constants of the equations are suitable if there is no possibility for the formation of a maximum or minimum.

Discussion of the individual equations

Examination of the Margules equation

The results of examining the binary Margules equation are summarized as follows.

According to the starting Margules equation:

$$\log \gamma_1 = x_2^2 [A + 2 x_1 (B - A)].$$

Substituting x for x_2 and $(1 - x)$ for x_1, and reducing the equation, the following equation is obtained:

$$\log \gamma_1 = 2 (A - B) x^3 + (2 B - A) x^2.$$

Deriving the equation with respect to x and making the derivate equal with 0:

$$\frac{d \log \gamma_1}{dx} = 6(A - B) x^2 + 2 (2 B - A) x = 0.$$

Solving the equation for x, according to the result an extreme value may exist at the value

$$x = \frac{A - 2 B}{3(A - B)} .$$

The value of x can vary from 0 to 1; therefore the following inequality can be written:

$$0 < \frac{A - 2 B}{3(A - B)} < 1.$$

Transforming and reducing the inequality, according to the result the necessary condition for the extreme value of curve log $\gamma = f(x)$ is the inequality

$$2A < B.$$

A condition of the correctness of the constants is an inequality of the opposite sense that is

$$2A > B$$

even mentioned by WOHL [3] and later by EBERT [4].

Examination of the Scatchard—Hamer-type equation

In case of the Scatchard—Hamer-type equation, the examination of the curves log $\gamma = f(x)$ and log $\gamma = f(z)$, respectively, can be executed in an analogous way.

According to the original equation,

$$\log \gamma_1 = A_{12} \left(\frac{2 A_{21} V_1}{A_{12} V_2} - 1 \right) z_2^2 - 2 A_{12} \left(\frac{A_{21} V_1}{A_{12} V_2} - 1 \right) z_2^3.$$

Substituting z for z_2 and $(1 - z)$ for z_1, and forming the derivative

$$\frac{d \log \gamma_1}{dz}$$

the extreme value is the following:

$$z = \frac{2 A_{21} V_1 - A_{12} V_2}{3 (A_{21} V_1 - A_{12} V_2)} .$$

However, for z the following inequality can be written:

$$0 < \frac{2 A_{21} V_1 - A_{12} V_2}{3 (A_{21} V_1 - A_{12} V_2)} < 1 .$$

Solving the inequality, as the condition for the existence of an extreme value the inequality

$$\frac{V_1}{V_2} > \frac{2 A_{12}}{A_{21}}$$

is obtained.

On the basis of the afore-said, the values of the constants are suitable if

$$\frac{2 A_{12}}{A_{21}} > \frac{V_1}{V_2} .$$

Examination of the modified Scatchard—Hamer-type equation

Recently, a modified Scatchard—Hamer-type equation was deduced for describing the vapour—liquid equilibria of systems strongly deviating from the ideal. This equation was deduced in connection with another problem [5]. This is as follows:

$$\log \gamma_i = 2\, z_i z_j^2 \frac{V_i}{V_j} A_{ji} + (z_j^3 - z_i z_j^2) \left(\frac{V_i}{V_j}\right)^2 A_{ij}\,.$$

Executing the substitutions employed as above, the following equation is obtained:

$$\log \gamma_i = 2 \left(\frac{V_i}{V_j}\right)^2 A_{ij} z^3 - \left(2 \frac{V_i}{V_j} A_{ji}\right) z^3 + 2 \frac{V_i}{V_j} A_{ji} z^2 - \left(\frac{V_i}{V_j}\right)^2 A_{ij} z\,.$$

Forming the first derivative with respect to z, the following expression is obtained for the extreme value:

$$z = \frac{\frac{V_i}{V_j} A_{ij} - 2\, A_{ji}}{3 \left(\frac{V_i}{V_j} A_{ij} - A_{ji}\right)}\,.$$

In the given case the following inequality is valid:

$$0 < \frac{\frac{V_i}{V_j} A_{ij} - 2\, A_{ji}}{3 \left(\frac{V_i}{V_j} A_{ij} - A_{ji}\right)} < 1\,.$$

Reducing this inequality, the condition for the existence of an extreme value is as follows:

$$\frac{A_{ji}}{2\, A_{ij}} < \frac{V_i}{V_j}\,.$$

Thus, the real values of the constants are determined by the following relation:

$$\frac{A_{ji}}{2\, A_{ij}} > \frac{V_i}{V_j}\,.$$

Summary

Computations were executed to determine the range of validity and the relation to each other of the constants of the binary three-suffix Margules, the Scatchard—Hamer-type and a modified Scatchard—Hamer-type equation deduced by the authors. As a result of the deduction the following limiting conditions were obtained:

Margules equation:

$$2\ \mathrm{A} > \mathrm{B}$$

Scathard—Hamer-type equation:

$$\frac{2\,A_{12}}{A_{21}} > \frac{V_1}{V_2}$$

Modified Scatchard—Hamer-type equation:

$$\frac{A_{ji}}{2\,A_{ij}} > \frac{V_i}{V_j}$$

The criteria thus obtained can be used to prove the unreliability of some equilibrium data and, if several data are available, also to select the most suitable value serving as the starting point for equilibrium computations.

Symbols used

x and x_2	molar fraction of the less volatile component in the liquid phase
x_1	molar fraction of the more volatile component in the liquid phase
z_i	effective volume fraction of component i in the liquid phase
A, B	constants of the Margules equation
A_{12}, A_{21}	constants of the Scatchard—Hamer-type equation
A_{ij}, A_{ji}	constants of the modified Scatchard—Hamer-type equation
V_i	actual molar volume of component i
γ_i	activity coefficient of component i

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Prof. Dr. J. Holló
Dr. T. Lengyel
A. Mészáros
Budapest, XI. Gellért tér 4. Hungary