Treatment of Isothermal x—y—P Equilibrium Data

E. GRACZOVÁ and J. SUROVÝ

*Department of Chemical and Biochemical Engineering, Faculty of Chemical Technology,
Slovak Technical University, SK-812 37 Bratislava*

The aim of this paper is to compare various types of objective functions for the treatment of the isothermal vapour—liquid (V—L) equilibrium data. The comparison is made for nine various x—y—P equilibrium data sets (exhibiting positive or negative deviations from ideal behaviour with and without azeotrope). From the results it is apparent that the objective function based on the maximum likelihood method offers the best results, the reproducibility of V—L equilibrium data has the best quality.

A number of authors [1—3] have attended to the problem of thermodynamic treatment of V—L equilibrium data. At present there are available papers as well as data banks, which apart from equilibrium data sets present also their thermodynamic treatment (*Gmehling* and *Onken* [4], *Hirata et al.* [5], *etc.*). These authors usually have used for the evaluation of parameters involved in equations for the excess Gibbs energy (G^E equations) various forms of objective functions.

Gmehling and *Onken* [4] employed the objective function based on activity coefficients

$$F = \sum_n \left(\frac{\gamma_1 - \gamma_{\mathrm{calc},1}}{\gamma_1} \right)^2_n + \sum_n \left(\frac{\gamma_2 - \gamma_{\mathrm{calc},2}}{\gamma_2} \right)^2_n$$

$$n = 1, 2, \ldots N \qquad (1)$$

where γ_i and $\gamma_{\mathrm{calc},i}$ denote measured and calculated activity coefficients of component i, respectively.

Hirata et al. [5] adopted an excess objective function in the form

$$F = \sum_n (Q - Q_{\mathrm{calc}})^2_n \quad Q = \frac{G^E}{RT} \qquad (2)$$

Orye and *Prausnitz* [6] used the pressure function

$$F = \sum_n \left(\frac{P - P_{\mathrm{calc}}}{P} \right)^2_n \qquad (3)$$

and *Tassios* [7] applied a function in the following form

$$F = \sum_n (y_1 - y_{\mathrm{calc},1})^2_n + \sum_n (y_2 - y_{\mathrm{calc},2})^2_n$$

$$+ \sum_n \left(\frac{P - P_{\mathrm{calc}}}{P} \right)^2_n \qquad (4)$$

Here y_i and $y_{\mathrm{calc},i}$ are measured and calculated mole fractions of the component i in the vapour phase, respectively.

The result of utilization of various objective functions are different values of the parameters of G^E equations as well as qualitatively different reproducibility of equilibrium V—L data treated.

Starting from the maximum likelihood method, which expresses the statistical behaviour of random errors of all measured quantities, the following function for the isothermal set of the x—y—P equations was used

$$F = \sum_n (x_1 - x_{\mathrm{calc},1})^2_n + \sum_n (y_1 - y_{\mathrm{calc},1})^2_n$$

$$+ \sum_n \left(\frac{P - P_{\mathrm{calc}}}{P} \right)^2_n \qquad (5)$$

This function incorporates, apart from dependent variables y and P, also an independent variable x, *i.e.* the mole fraction of the component in the liquid phase. For the minimization of the objective function (5) we used an iteration method, including two iteration cycles.

In the first cycle, a set of equations created from the conditions

$$\left(\frac{\partial F}{\partial A_r} \right)_{A_{q \neq r}, x_1} = 0 \qquad r = 1, 2, \ldots R \qquad (6)$$

is solved. The solution offers the first approximation of coefficients of G^E equations – A_r.

In the second cycle, by solving conditions

$$\left(\frac{\partial F}{\partial x_1} \right)_{A_r} = 0 \qquad (7)$$

the most probable x_1 are calculated, separately for each experimental point. The alteration of both the cycles is repeated until the difference of values of both the adjacent iterations is smaller than the tolerance

required. For the calculation of $x_{\text{calc},1}$ we suggested the iteration calculation in the minimum of the objective function (5). From condition (7), it holds

$$\left(\frac{\partial F}{\partial x_1}\right)_{A_r} = 0 = (x_1 - x_{\text{calc},1})$$
$$+ (y_1 - y_{\text{calc},1})\left(\frac{\partial y_{\text{calc},1}}{\partial x_1}\right) \qquad (7a)$$
$$+ \left(\frac{1}{P^2}\right)(P - P_{\text{calc}})\left(\frac{\partial P_{\text{calc}}}{\partial x_1}\right)$$

If one considers that approximately

$$y_1 = y_{\text{calc},1}^{\circ} + \left(\frac{\partial y_{\text{calc},1}}{\partial x_1}\right)^{\circ} \Delta x_1$$

$$y_{\text{calc},1}^{\circ} = y_1(x_1 = x_{\text{calc},1}^{\circ}) \qquad (8)$$

$$P_{\text{calc}} = P_{\text{calc}}^{\circ} + \left(\frac{\partial P_{\text{calc}}}{\partial x_1}\right)^{\circ} \Delta x_1$$

$$P_{\text{calc}}^{\circ} = P(x_1 = x_{\text{calc},1}^{\circ}) \qquad (9)$$

$$x_{\text{calc},1} = x_{\text{calc},1}^{\circ} + \Delta x_1 \qquad (10)$$

then, for the increment Δx_1 of the n-th measurement one can derive the following expression

$$\Delta x_1 = \frac{(x_1 - x_{\text{calc},1}^{\circ}) + (y_1 - y_{\text{calc},1}^{\circ})\left(\frac{\partial y_{\text{calc},1}}{\partial x_1}\right)^{\circ} + \left(\frac{1}{P^2}\right)(P - P_{\text{calc}}^{\circ})\left(\frac{\partial P_{\text{calc}}}{\partial x_1}\right)^{\circ}}{1 + \left(\frac{\partial y_{\text{calc},1}}{\partial x_1}\right)^{\circ 2} + \left(\frac{1}{P^2}\right)\left(\frac{\partial P_{\text{calc}}}{\partial x_1}\right)^{\circ 2}} \qquad (11)$$

By the superscripts $^{\circ}$ are denoted the values from the last iteration.

RESULTS AND DISCUSSION

Objective functions $(3—5)$ were applied for binary systems exhibiting a positive deviation from ideal solution (toluene—aniline, $\theta = 90\,^{\circ}\text{C}$; ethyl benzene—aniline, $\theta = 80\,^{\circ}\text{C}$; cyclohexane—methylcyclohexane, $\theta = 35\,^{\circ}\text{C}$), or a negative deviation from ideal behaviour (hexafluorobenzene—xylene, $\theta = 50\,^{\circ}\text{C}$; tetrachloromethane—methylcyclohexane, $\theta = 50\,^{\circ}\text{C}$) all without azeotrope and azeotropic systems (ethanol—benzene, $\theta = 40\,^{\circ}\text{C}$; 1-hexyne—acetonitrile, $\theta = 45\,^{\circ}\text{C}$; benzene—cyclohexane, $\theta = 49\,^{\circ}\text{C}$; benzene—*tert*-butanol, $\theta = 25\,^{\circ}\text{C}$). (Experimental sets of the above-mentioned systems are given in the data bank DECHEMA, Ref. [4].) The following objective function based on mole fractions y

$$F = \sum_n (y_1 - y_{\text{calc},1})^2_n \qquad (12)$$

was utilized to supplement and illustrate the different reproducibility of $x—y—P$ equilibrium data.

The results of thermodynamic treatment were compared with the results presented in DECHEMA (where the authors of [4] used the objective function (1)). For the sake of computation of P and/or mole fractions of the component in the vapour phase y_i, relationships were used taking into account the ideal behaviour of the vapour and real behaviour of the liquid phase. For the calculation of activity coefficients we chose G^{E} equations with two parameters – van Laar and Wilson equations and with three parameters – NRTL and the fourth-order Redlich—Kister equations. Results of calculations are summarized in Table 1, where the mean and standard deviations of variables P, y and/or x separately for each G^{E} equation are given. Data in Table 1 were calculated as the arithmetical mean of deviations for all nine systems. From this table it is evident that for a thermodynamic treatment one uses an objective function on the basis of pressures (3), the reproducibility of pressure becomes better to the detriment of reproducibility of mole fraction y (mean deviation of pressure $d(P) = 0.104$ kPa, mean deviation of mole fraction $d(y) = 0.0075$). An analogical situation is in the case of employment of the objective function on the basis of mole fractions (12): $d(y) = 0.0051$, where $d(P) = 0.307$ kPa. From the comparison of the objective functions (1), (4), and (5) it is apparent that the best results are obtained by the objective function (5), for which the mean deviations of variables are $d(P) = 0.071$ kPa, $d(y) = 0.0045$, and $d(x) = 0.0033$. In the case of the employment of the objective function (4) the mean deviations of pressure and mole fraction are higher: $d(P) = 0.112$ kPa, $d(y) = 0.0069$. Deviation of mole fraction y is in the case of utilization of the objective function (1) comparable with the objective function (4), deviation of pressure is almost three times higher, $d(P) = 0.297$ kPa.

SYMBOLS

A_r coefficient of the equation for the excess Gibbs energy
d mean deviation
F objective function
G^{E} molar excess Gibbs energy
n number of measurements
N total number of measurements

Table 1. Mean and Standard Deviations of Pressures, Mole Fractions in Vapour and Liquid (of the all above-mentioned systems) for Various Types of Objective Functions F

F	$d(P)/\text{kPa}$	$s(P)/\text{kPa}$	$d(y)$	$s(y)$	$d(x)$	$s(x)$
Van Laar equation						
(1)	0.324	0.370	0.0072	0.0088		
(3)	0.115	0.144	0.0081	0.0097		
(4)	0.121	0.156	0.0075	0.0091		
(5)	0.076	0.095	0.0048	0.0056	0.0035	0.0043
(12)	0.317	0.357	0.0056	0.0063		
Wilson equation						
(1)	0.287	0.326	0.0062	0.0076		
(3)	0.105	0.133	0.0073	0.0086		
(4)	0.112	0.133	0.0068	0.0080		
(5)	0.077	0.092	0.0047	0.0062	0.0032	0.0041
(12)	0.303	0.340	0.0050	0.0057		
NRTL equation						
(1)	0.279	0.327	0.0068	0.0083		
(3)	0.106	0.142	0.0079	0.0093		
(4)	0.111	0.155	0.0073	0.0086		
(5)	0.074	0.092	0.0046	0.0057	0.0035	0.0044
(12)	0.316	0.367	0.0051	0.0060		
Redlich—Kister equation						
(1)	a					
(3)	0.091	0.116	0.0068	0.0083		
(4)	0.104	0.131	0.0061	0.0064		
(5)	0.057	0.070	0.0037	0.0046	0.0030	0.0038
(12)	0.291	0.332	0.0048	0.0055		

a) Not published by DECHEMA.

P total pressure
Q excess function
R gas constant
R total number of coefficients in the equation for the excess Gibbs energy
s standard deviation
T absolute temperature
x_i mole fraction of component i in liquid
y_i mole fraction of component i in vapour
γ_i activity coefficient of component i
θ temperature

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