

## VAPOUR-PHASE NON-IDEALITY IN LOW-PRESSURE VAPOUR-LIQUID EQUILIBRIUM DATA CORRELATION

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The effect of vapour-phase imperfections and the volumetric behaviour of liquid phase on the low-pressure VLE data reduction was investigated. The errors in the vapour-phase composition due to processing experimental data assuming ideal behaviour of the vapour phase were evaluated.

A large part of chemical industry is concerned with separation operations such as distillation and rectification. For rational design of the separation processes as well as for the determination of optimum operation of the separation units, we require quantitative information on phase equilibria and especially on vapour-liquid equilibria.

One of the main problems of vapour-liquid equilibrium data processing is their reduction to a small number of theoretically significant functions and parameters. The experimental vapour-liquid equilibrium data on binary systems are usually correlated by means of suitable equations and the constants obtained are used for predicting the equilibrium behaviour of industrially important multicomponent mixtures. For accurate data reduction and for the prediction of multicomponent vapour-liquid equilibria, the vapour-phase non-ideality should be taken into account.

This paper deals with the effect of vapour-phase nonideality on the quality of correlation of experimental vapour-liquid equilibrium data. The chosen set of systems treated includes isothermal binary systems ranging from ideal to strongly non-ideal ones. The total vapour pressures in the systems studied are below or equal normal atmospheric pressure (in most cases 55–105 kPa). The systems containing strongly associating components (especially fatty acids) are not considered.

### *Thermodynamic Relations*

For two phases, vapour V and liquid L, the equation of equilibrium for each component  $i$  can be expressed<sup>1</sup> in terms of the fugacity  $f$  as

$$f_i^V = f_i^L \quad (1)$$

On taking the usual standard state, *i.e.* that of pure component at the system temperature and pressure, we can derive, by a standard thermodynamic procedure<sup>2</sup>, an exact relation expressing the dependence of state variables in a system consisting of the liquid and vapour phases at equilibrium in the form

$$\gamma_i = [(y_i P)/(x_i P_i^0)] Z_i, \quad (2)$$

where  $\gamma_i$  is the activity coefficient,  $y_i$  and  $x_i$  stand for the mole fraction of component  $i$  in the vapour and liquid phase, respectively,  $P$  is the system pressure,  $T$  the system temperature,  $P_i^0$  the saturated pressure of pure component  $i$  and  $Z_i$  is a correction factor for the volumetric behaviour of the vapour and liquid phases. A general expression for  $Z_i$  takes the form

$$Z_i = (\varphi_i/\varphi_i^0) \exp\left(-\int_{P_i^0}^P (V_i/RT) dP\right), \quad (3)$$

where  $\varphi_i$  and  $\varphi_i^0$  is the fugacity coefficient of component  $i$  in the mixture and of pure component  $i$  at saturation, respectively,  $V_i$  is the molar volume of pure liquid  $i$  and  $R$  the gas constant. On the assumption that at low pressures the virial equation of state truncated after the second virial coefficient,

$$PV/RT = 1 + BP/RT, \quad (4)$$

provides a satisfactory representation of the volumetric properties of vapour mixtures and that the molar volume of the pure liquid component is independent of pressure, we can arrive at the final equations for activity coefficients in binary solutions

$$\ln \gamma_1 = \ln (y_1 P)/(x_1 P_1^0) + [(B_{11} - V_1)(P - P_1^0) + P\delta_{12}y_2^2]/RT, \quad (5a)$$

$$\ln \gamma_2 = \ln (y_2 P)/(x_2 P_2^0) + [(B_{22} - V_2)(P - P_2^0) + P\delta_{12}y_1^2]/RT, \quad (5b)$$

where

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \quad (6)$$

and  $B_{ii}$  is the second virial coefficient of the  $i$ -th component,  $B_{ij}$  the second cross virial coefficient.

Eqs (5a)–(6) allow to calculate the true liquid phase activity coefficients for binary solutions from vapour–liquid equilibrium data and a minimum of volumetric information. Only in the case that the vapour phase behaves ideally, the last term in Eqs (5a) and (5b) becomes insignificant and we get the well-known relation

$$\gamma_i = (y_i P)/(x_i P_i^0) \quad [*] \quad (7)$$

which is used very often for its simplicity.

### Data Correlation

From the thermodynamic point of view, the activity coefficients should be strictly evaluated using Eqs (5a) and (5b). In fact the simple Eq. (7) is used very often because the virial coefficients of pure components at conditions encountered in VLE at low pressures and especially the cross virial coefficients are available rather rarely. Even the up-to-date VLE data compilations such as the Gmehling and Onken monograph<sup>3</sup> do not apply a correction for the vapour-phase non-ideality. Maczyński in his collection<sup>4</sup> of VLE data uses in some cases the correction given by Eqs (5a) and (5b) but asserts that results of correlation are in most cases better when just the ideal vapour phase is considered. On the contrary, our previous investigations<sup>5</sup> showed that the first-rate quality data yielded better correlation when real vapour phase was taken into account.

In this context the question I wish eventually to consider is the following: What is the role of the above-mentioned correction in the data-treatment process and what error results from neglecting it?

The correlation of direct experimental VLE data does not provide a satisfactory quantitative answer<sup>5</sup> since the experimental data are subject more or less to random and especially to systematic errors and good virial coefficients are usually not available, too. The second way, *viz.* a thorough *a priori* mathematical analysis of the problem taking into account all the variables, their magnitudes and dependences would be inadequate, with respect to its complexity, to this purpose. Therefore we decided to employ a procedure based on "pseudoexperimental" data. The substance of the method is as follows: A number of suitable isothermal systems were selected (preferably those with total vapour pressures within 55–105 kPa) from three VLE data compilations<sup>3,4,6</sup> and saturated vapour pressures (in terms of the Antoine equation constants) and the Margules equation constants (1, 2 or exceptionally 3 with regard to non-ideality of the respective system) were taken over. The values of virial coefficients  $B_{ii}$  and  $B_{ij}$  were estimated mostly by the Hayden and O'Connell method<sup>7</sup> or in some cases by the O'Connell and Prausnitz method<sup>8</sup>. A set of  $x_i$  values was developed by means of the random number generator of a TI-59 calculator. Finally a program was written for computing VLE data by an iterative method from this information given. Now we can imagine that these semisynthetic data set represents measured values ( $x, y, P$  at given  $T$ ) for some real system. Naturally, they need not reproduce exactly the original data.

To find the effect of the correction for the vapour-phase non-ideality we can now correlate our "pseudoexperimental" data, which are perfect from the thermodynamic

point of view, assuming ideal vapour phase. Since our aim is to provide data for chemical engineers we used the recommended<sup>9</sup> objective function  $F$  suitable for the determination of the number of stages of distillation equipment, *viz.* the difference of logarithms of the ratios of activity coefficients

$$F = \sum [\ln (\gamma_1/\gamma_2)_{\text{exp}} - \ln (\gamma_1/\gamma_2)_{\text{calc}}]^2 . \quad (8)$$

The constants of the correlation equations were obtained by the least-square minimization of the function  $F$ .

The concentration dependence of activity coefficients was expressed by means of the Margules 3rd order equation<sup>2</sup>

$$\log (\gamma_1/\gamma_2) = x_2^2 A_{12} - x_1^2 A_{21} - 2x_1 x_2 (A_{12} - A_{21}) , \quad (9)$$

and the Margules 4th order equation<sup>2</sup>

$$\log (\gamma_1/\gamma_2) = x_2^2 A_{12} - x_1^2 A_{21} - 2x_1 x_2 [A_{12} - A_{21} + (x_2 - x_1) D_{12}] , \quad (10)$$

where  $A_{12}$ ,  $A_{21}$ ,  $D_{12}$  are constants characteristic of the given mixture and equation.

To compare the results of correlation we used two criteria, *viz.* the average deviation in the vapour phase composition

$$\text{Avg} = \sum |y_{\text{ideal v.p.}} - y_{\text{real v.p.}}|/n \quad (11)$$

and the bias as a measure of systematic deviations (inconsistency) of data

$$\text{Bias} = \sum (y_{\text{ideal v.p.}} - y_{\text{real v.p.}})/n , \quad (12)$$

where  $n$  is the number of experimental points.

## DISCUSSION

More than 140 isothermal systems were employed covering wide range of non-ideality from nearly ideal to strongly non-ideal systems and pertaining to different combinations of groups of the Ewell's classification of liquids (excepting the systems containing fatty acids).

The isothermal VLE data were preferred for the temperature dependence of input parameters ( $A_{ij}$ ,  $B_{ij}$ ,  $B_{ij}$  and  $V_i$ ) did not have to be considered. On the other hand, the deviations  $\Delta y$  are dependent on the system temperature and total pressure. Even though we selected preferably the systems whose total pressure was within 55–105 kPa, some conversion seemed to be desirable. To allow for the effect of tem-

perature (pressure) the simple linear dependence

$$\Delta y = (\Delta y)_{\text{calcd}}(101/\bar{P}^0) \quad (13)$$

TABLE I

Effect of Temperature and Pressure on Deviation ( $\Delta y$ ) Due to Vapour-Phase Non-Ideality (the ethanol-toluene isothermal systems)

$t, ^\circ\text{C}$	$(\Delta y)_{\text{calc}} \cdot 10^4$	$P_1^0, \text{kPa}$	$P_2^0, \text{kPa}$	$\Delta y \cdot 10^4$ <sup>a</sup>
35	5	13.8	6.24	50
50	10	29.5	12.3	48
55	13	37.3	15.1	50
60	16	46.9	18.5	49
65	20	58.4	22.5	50
70	24	72.2	27.2	49
75	28	88.7	32.6	47
80	34	108.2	38.8	47
85	40	131.2	46.0	46

$$^a \Delta y = (\Delta y)_{\text{calc}} \cdot 2 \cdot 101 / (P_1^0 + P_2^0).$$

TABLE II

Effect of Vapour-Phase Non-Ideality on the Correlation of VLE Data of Isothermal Systems

System type	Number of systems	$\Delta y_{\text{mean}} \cdot 10^4$ <sup>a</sup>	$\Delta y_{\text{max}} \cdot 10^4$ <sup>a</sup>
Hydrocarbon-hydrocarbon	18	42	105
Hydrocarbon-alcohol	35	26	49
Hydrocarbon-halogenated hydrocarbon	12	17	30
Halogenated hydrocarbon-alcohol	26	30	68
Ester-alcohol	8	46	93
Alcohol-water	5	25	40
Alcohol-alcohol	5	65	87
Acetone-miscellaneous	14	53	89
Aniline-hydrocarbon	4	36	39
Miscellaneous systems	16	84	110
<i>Overall</i>	<i>143</i>	<i>40</i>	

<sup>a</sup>  $\Delta y$  Values are converted to 101 kPa in terms of Eq. (13).

proved to be sufficient for the comparatively narrow pressure range. Here  $\bar{P}^0$  is the average of saturated vapour pressures of components in kPa, i.e.  $\bar{P}^0 = (P_1^0 + P_2^0)/2$ , and  $(\Delta y)_{\text{calc}}$  is the value computed under the conditions of the respective system. The utility of the conversion to the chosen pressure of 101 kPa is illustrated in Table I.

The results of the work proved that 1) The correlation of VLE data assuming ideal vapour-phase behaviour brings about a shift of data, i.e. the data appear to be thermodynamically inconsistent. It follows from the fact that the criteria Avg and Bias are numerically identical. 2) Owing to the inconsistency, no improvement is obtained when the initial number of the Margules constants (1 or 2) is increased by another one. 3) No obvious correlation was traced of  $\Delta y$  with the liquid-phase non-ideality. The ideal systems show deviations of comparable magnitude with the non-ideal ones.

The quantitative results of the test are summarized in Table II. Limits of errors due to neglecting the  $P$ - $V$ - $T$  behaviour of the vapour and liquid phase can be found there. The values of deviations are believed to be representative, at least as to the order of magnitude, of other objective functions and/or correlation relations, too.

In summary, I would like to emphasize: The correction for the vapour-phase non-ideality should be applied whenever possible. Its neglecting results in the thermodynamic inconsistency of data treatment which cannot be compensated by adding further constants in the correlation relations for activity coefficients. The errors in the vapour-phase composition due to this effect are within several tenths up to one mol per cent.

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