# VAPOUR-LIQUID EQUILIBRIUM CORRELATION PROCEDURE IN HIGH PRESSURE REGION*

Ivan WICHTERLE
*Institute of Chemical Process Fundamentals,*
*Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchdol*

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*Dedicated to Professor E. Hála on the occasion of his 60th birthday.*

A new procedure is proposed for evaluation of binary interaction parameters required for the Redlich-Kwong-Soave method of calculation of high pressure vapour-liquid equilibria.

There exist two large problems related to any evaluation procedure of vapour-liquid equilibrium data, namely *1*) the choice of the objective function to be minimized, and *2*) the selection of criteria which would indicate the quality of correlation. A great amount of procedures can be created by combining the variety of both items, however, only one of them can be applied finally. Therefore, the evaluation procedure is often found beforehand and the testing data are carefully selected in order to demonstrate as best as possible the results, indicating so the quality of data or calculation procedure proposed. From among the criteria available, those yielding worse results are sometimes simply omitted.

Everybody who has to deal with correlation knows that the final result can be easily manipulated or controlled by properly selected both the objective function and the evaluation procedure. In addition, the average or standard deviations of certain property in whatever way excellent may hide very poor results obtained for other quantities. For instance, the deviation in composition of vapor phase is frequently selected to be a measure of the quality of curve fitting. One may consider the average absolute deviation 0·5 mol% as very good one. However, at compositions higher than 98%, such a deviation causes at least an 25—40% error and on the average an 35—100% error in the *K*-value of less volatile component. This is not uncommon case, *e.g.* in the methane-butane system at 200 K such compositions occur within pressures 1—6 MPa which represent 80% of available pressure range. Moreover, this criterion discriminates the low concentrations at all.

Even if a certain objective function and criteria are found, the routine for their evaluation is neither simple nor easy. The computation of one vapour-liquid equi-

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librium point at high pressures represents a complex iterative procedure which need not necessarily converge to the solution. Therefore, during the trial-and-error adjustment the number of points evaluated together is randomly varying. In other words, the objective function calculated by means of supposedly better parameters gives a worse result comparing it with a previous approximation because the number of data input had to be changed due to the convergency difficulties.

Fortunately most of vapour--liquid equilibrium calculation procedures at high pressure have more predictive than correlation character, *i.e.* they use only the pure property data and binary parameters without any additional correlation. However, the correlation must be carried out when the binary interaction constants are evaluated.

The imperfections of $\Delta y$ criterion has been already mentioned. Analogously the selection of $\Delta P$ does not solve the problem. It can be shown that in many cases when this criterion is used for the minimization, the deviations in phase concentrations are very poor. Sometimes the deviations in $K$-values are recommended, even though the percent deviations look infavourably worse comparing them with the above-mentioned criteria. Moreover, this procedure disregards the pressure completely.

From among the available variables $x$, $y$, $P$, and $T$ two of them only are independent. Then, we are facing the problem how to evaluate this group of four to be as close as possible to the experimental point. There are six independent combinations which can be used for evaluation, but altogether can be substituted by the maximum likelihood procedure. This method is rather complicated and time-consuming and this is the reason why it has not been widely used.

The most widespread procedure is the dew-point – pressure calculation $(y - P)$, which considers the exact temperature and liquid phase composition, discriminating so the vapour composition data. This process can be reversed; then the bubble-point – pressure evaluation $(x - P)$ is carried out. On the contrary, such procedure discriminates the liquid composition data. Nevertheless, two independent (different as a rule) values of pressure are obtained with use of the both methods mentioned above. For these types of computation the remaining state quantity ($T$ for isothermal or $P$ for isobaric data) is considered as exact one, which is very correct comparing its accuracy with that of the composition data.

The method can be used perhaps for low pressure evaluations but for the systems with one supercritical component fails in some extent. During the $y - P$ calculation in the region of rounded $x, y - P$ curve two solutions for pressure exist which cannot be distinguished unless the computation is carried out for the whole curve.

## THEORETICAL

To avoid this difficulty a simple method has been proposed that does not require the knowledge of analytical correlation function (in contrast with the maximum likelihood method). Two independent evaluation procedures (usually the computations of $y - P$ and $x - P$ type) are used to obtain two points calculated in the neighborhood of a particular experimental point. These calculated points are used consequently for linear representation of any relation between two variables or related quantities, *e.g.* $x - P$, $K - P$, *etc.* Then, the shortest distance of an experimental point from this line indicates the quality of fit. It is defined as a distance measured along the normal line (perpendicular) to the linear representation. Since the variables are measured with different accuracy the slope of the normal line must be multiplied by the ratio of their variances[1]. Here for instance, two independent pressures are obtained from $x - P$ and $y - P$ curves. Subsequently, their average value is used for the flash type calculation to get the both phase compositions. By use of this procedure (illustrated in Fig. 1) all the deviations can be evaluated except for one ($T$).

As the selection of the objective function concerns, many of them have been suggested and investigated for low pressure correlations[2,3]. Nevertheless, only few of them have been applied to high pressure evaluations. Most frequently the square deviations in pressure or in $K$-values are used. The former one is preferred even though

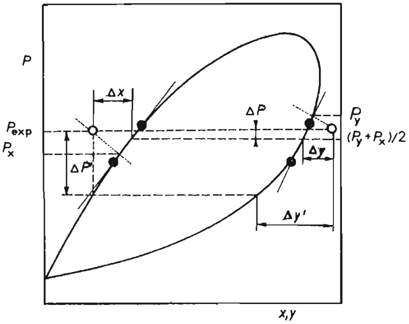

FIG. 1

Evaluation of Deviations

○ Experimental points, ● correlated points close to experiment; ——— correlation; $\Delta P'$, $\Delta y'$ deviations evaluated using the dew-point – pressure method; $\Delta P$, $\Delta y$, $\Delta x$ deviations evaluated using the proposed method.

TABLE I

Binary Parameters and Corresponding Deviations

| System | Procedure[a] | $k_{ij}$ | $\Delta P$ | $\Delta y$ | $\Delta x$[b] |
|---|---|---|---|---|---|
| Methane–ethane | A | −0·0051 | 3·19 | 1·92 | — |
| | B | −0·0067 | 1·41 | 0·59 | 0·24 |
| Methane–propane | A | 0·0078 | 2·53 | 0·19 | — |
| | B | 0·0093 | 1·88 | 0·29 | 1·11 |
| Ethane–propane | A | −0·0072 | 0·89 | 0·48 | — |
| | B | 0·0008 | 1·28 | 0·36 | 0·20 |
| Ethane–butane | A | 0·0283 | 1·42 | 1·06 | — |
| | B | 0·0224 | 0·84 | 0·69 | 0·75 |
| Ethane–isobutane | A | 0·0001 | 3·43 | 2·14 | — |
| | B | −0·0014 | 1·34 | 0·78 | 0·45 |
| Propane–butane | A | 0·0105 | 1·02 | 2·90 | — |
| | B | −0·0033 | 0·69 | 1·78 | 1·81 |
| Ethylene–ethane | A | 0·0079 | 0·42 | 0·21 | — |
| | B | 0·0075 | 0·41 | 0·12 | 0·11 |
| Propylene–propane | A | 0·0034 | 0·48 | 0·39 | — |
| | B | 0·0037 | 0·49 | 0·19 | 0·20 |
| Propylene–isobutane | A | −0·0167 | 3·17 | 1·18 | — |
| | B | −0·0195 | 2·96 | 0·67 | 0·62 |
| Propane–benzene | A | 0·0269 | 3·89 | 1·27 | — |
| | B | 0·0247 | 1·78 | 0·75 | 0·68 |
| Nitrogen–methane | A | 0·0322 | 15·4 | 4·16 | — |
| | B | 0·0280 | 14·6 | 3·88 | 1·01 |
| Nitrogen–ethylene | A | 0·0734 | 5·92 | 1·72 | — |
| | B | 0·0758 | 0·57 | 1·19 | 0·55 |
| Carbon monoxide–methane | A | 0·0061 | 1·40 | 0·52 | — |
| | B | 0·0063 | 0·96 | 0·27 | 0·33 |
| Argon–methane | A | 0·0106 | 0·63 | 1·10 | — |
| | B | 0·0196 | 1·40 | 0·56 | 0·24 |
| Carbon dioxide–ethylene | A | 0·0602 | 0·52 | 0·44 | — |
| | B | 0·0597 | 0·69 | 0·88 | 0·89 |
| Carbon dioxide–propane | A | 0·1245 | 7·30 | 3·17 | — |
| | B | 0·1329 | 0·55 | 0·46 | 0·41 |

[a] A dew-point — pressure evaluation, B proposed method, [b] $\Delta P$ mean per cent deviation in pressure, $\Delta y$ mean deviation in composition of vapour phase (mol %), $\Delta x$ mean deviation in composition of liquid phase (mol %).

in many cases both objective functions compete in a contradictive manner, making difficult to find out their optimum proportion.

With regard to the above-mentioned procedure for the determination of deviations, several objective functions were examined, *e.g.* sum of $\Delta^2 P$, sum of distances from $x - P$ and $y - P$ curve, sum of distances from $P - K_1$ and $P - K_2$ in logarithmic scales, *etc.* No substantial differences have been found among these functions, except for the $\sum \Delta^2 P$, yielding relatively the best deviation in pressure.

## RESULTS

The correlation was carried out on using the Redlich–Kwong equation of state as modified by Soave[4]. The objective function represented by the sum of square deviations in pressure was evaluated in the optimization procedure described above which was applied to 16 systems containing aliphatic, olefinic or aromatic hydrocarbons, nitrogen, CO, $CO_2$ and Ar.

The comparison with the common dew-point – pressure calculation shows that a better description of high pressure vapour–liquid equilibrium is attained with the interaction parameter evaluated by means of the proposed procedure. On the average, the error in pressure is improved from 3·46 to 2·09%, and in vapour phase composition from 1·39 to 0·83 mol %. While the dew-point – pressure method misinterprets the accuracy of liquid phase composition (error equals to zero), the proposed method indicates the error in liquid composition (0·65 mol %) which is comparable with that for vapour phase. This fact has also favourable averaging effect on the errors in $K$-values: (higher) error in $K_1$ decreases from 7·8 to 6·8% and (lower) error in $K_2$ increases from 3·5 to 3·9%. The adjusted interaction parameters $k_{12}$ are presented in Table I with the corresponding errors.

## DISCUSSION

Liquid composition must not be preferred to vapour one and *vice versa* and the pressure must not be discriminated with regard to composition. With respect to these facts, the maximum proximity method was proposed and used for simultaneous evaluation of all variable deviations except that which is kept constant ($T$ or $P$). This approach represents a very simplified maximum likelihood method and it is especially designed for the high pressure vapour–liquid equilibria, where the importance of pressure is dominant, and for systems with one supercritical component. For those cases the maximum likelihood method is practically unfeasible. The presented approach can be applied to any evaluation of binary parameters required in any calculation method for high pressure vapour–liquid equilibrium.

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