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Use of Concentration Pulse Chromatography for Determining Binary Isotherms: *Comparison with Statically Determined Binary Isotherms*

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Abstract. The characterization of adsorption properties of binary gas mixtures is an important factor in the design of cyclic periodic adsorption processes. Presently, there are a few methods for determining the binary adsorption behaviour. However, most of these methods are very time demanding (static approaches). One dynamic approach for determining the binary adsorption behaviour is by employing the concentration pulse method. Although this experimental method has been shown to reliably reproduce the data obtained with static approaches, the application has been limited to systems where the adsorption capacities are similar. In our previous work, a novel method (HT-CPM) was shown to be capable of handling systems where the adsorption capacity of the heavy component is much greater than the light component.

In order to further validate the novel method, HT-CPM, previously published statically determined binary adsorption data have been used to supply the data required for the concentration pulse method (CPM) data reduction techniques. From this data, the HT-CPM was then applied and the resulting data compared. The two other CPM approaches were also applied and these results are shown.

Four binary systems were chosen so that a range of heavy/light adsorption capacities was examined. The results show that the HT-CPM was able to produce results that were consistent with the static data taken from the literature. The other data reduction techniques used with the CPM could only produce meaningful data when the adsorption capacities of the heavy and light components were similar.

Keywords: adsorption, equilibrium, binary isotherms, multi-component, HT-CPM, concentration pulse method

Introduction

The use of adsorption based gas separations for industrial processes are widespread. The developments of new adsorbents for these separations are also evolving rapidly. This growth facilitates the need to characterize the adsorbents for a very large subset of gases (Farla et al., 1995). One dynamic method of analysis is by use of the chromatographic technique. This method can be employed in several ways; tracer gas, step change, and pulse chromatography. In this study, concentration pulse chromatography has been employed (Shah and Ruthven, 1977; Van der Vlist and Van der Meijden, 1973; Ruthven and Kumar, 1980; Hyun and Danner, 1982; Tezel et al., 1992; Harlick and Tezel, 2000, 2001, 2002).

The use of concentration pulse chromatography for adsorbent screening is very attractive since it is relatively inexpensive to set-up. Further, this method is capable of characterizing adsorbents quicker than other methods presently used. However, presently available methods for determining binary isotherms from concentration pulse method (CPM) data for highly selective adsorbents are not applicable (Harlick and Tezel, 2000). A novel solution method for determining binary isotherms from concentration pulse chromatography data, the Harlick-Tezel Concentration Pulse Method (HT-CPM), was developed in our earlier work (2000, 2001, 2002). This method proved to be able to handle binary adsorption systems where the components

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exhibit large differences in their adsorption capacity. Further, this method was described to be able to incorporate any functional form that can fit the experimental data. This attribute makes this method more versatile than the polynomial VV-CPM (Van der Vlist and Van der Meijden Concentration Pulse Method) (Van der Vlist and Van der Meijden, 1973), or the functional form developed by Triebe and Tezel (1995), TT-CPM (Triebe and Tezel Concentration Pulse Method).

The purpose of this study was to determine the applicability of the HT-CPM in comparison to statically determined binary adsorption data from the literature. A total of four binary systems were chosen and reduced to binary K_p data for use with the CPM. The CPM was scrutinized with the use of the VV-CPM, TT-CPM and HT-CPM approaches for the data reduction task.

For this study, the binary adsorption systems were chosen from the available literature data, so that a range of heavy/light adsorption capacities could be studied. The target range was for systems that exhibit similar to weak adsorption capacity ratios. The following systems were chosen:

(1) CH_4-CO_2 AC (Golden and Sircar, 1994)
(2) CO_2-C_2H_4 13X (Hyun and Danner, 1982)
(3) C_2H_4-C_2H_6 13X (Danner and Choi, 1978; Hyun and Danner, 1982)
(4) CO-O_2 5A (Sircar, 1991; Danner and Wenzel, 1969)

From these systems, a range of binary adsorption behavior was examined.

Background and Literature Review

With Concentration Pulse Method (CPM), a pulse of sample is injected into the carrier gas stream and passes through an adsorbent packed column. The response of the column to the injection is measured as concentration vs. time at the exit of the column. From this response peak a mean retention time of the sample, μ, is determined experimentally:

$$\mu = \frac{\int_0^\infty c\,(t - \mu_D)\,dt}{\int_0^\infty c dt} \tag{1}$$

The term μ_D is the mean system dead time. This dead time is the measure of the time required for a sample pulse to travel through the empty volume of the interconnecting tubing from injection point to the detector, and void space in the packed column.

At that carrier gas composition the mean retention time is related to the effective isotherm slope, K, by Eq. (2) (Shah and Ruthven, 1977; Van der Vlist and Van der Meijden, 1973; Ruthven and Kumar, 1980; Hyun and Danner 1982; Tezel et al., 1992; Triebe and Tezel, 1995; Harlick and Tezel, 2000, 2001, 2002):

$$\mu = \frac{L}{v}\left[1 + \frac{(1-\varepsilon)}{\varepsilon}K\right]$$
$$K_p(\text{Dimensional}) = K(\text{Dimensionless}) \times \frac{RT}{\rho_p} \tag{2}$$

The system dependent constant $\frac{RT}{\rho_p}$ is the conversion factor for transforming the dimensionless K to the dimensional K_p. The K_p value is related to the slopes of the mixture isotherms of each component in the carrier gas mixture. For a binary mixture, the relationship is given as follows:

$$K_p(\text{Experimental}) = (1 - y_1)\frac{dq_1}{dP_1} + y_1\frac{dq_2}{dP_2} \tag{3}$$

where, $\frac{dq_1}{dP_1}$ and $\frac{dq_2}{dP_2}$ are the slopes of the adsorption isotherms for components 1 and 2, respectively.

For binary isotherms, both components in the mixed carrier gas are adsorbed. Therefore, the experimental K_p data represent the combined contribution of both components. The interpretation of the binary K_p data has been treated by several methods (Van der Vlist and Van der Meijden, 1973; Buffman et al., 1985, 1999; Triebe and Tezel, 1995; Kabir et al., 1998; Tezel et al., 1992).

The method of Kabir et al. (1998) is based on determining the activity coefficients from the binary retention time data. For ideal mixtures, these values are related to Ideal Adsorbed Solution Theory suggested by Myers and Prausnitz (1965). For the case of non-ideal mixtures, the use of the Regular Solution Model was used. Both of these approaches allow for the determination of binary adsorption isotherms. However, the extent of their applicability is related to the degree of the fit of the binary K_p data.

For the method of Buffman et al. (1985), a retention time is related to each of the flow-rate and concentration transients at the outlet. These transients are then related to the phase behavior of the mixture. From this information, the slopes of the isotherms are found. This

method was furthered by Mason and Buffman (1996) to include the effects of pressure changes.

Another approach was developed by Buffman et al. (1999). In this method, a form for the binary isotherms is assumed and the corresponding K_p function is determined. Although Buffman et al. used the binary Langmuir isotherm for illustration purposes; any binary isotherm model can be used. With this approach, a well-established isotherm model is applied. However, not all binary adsorption systems may follow the chosen model. This can be seen by the quality of the experimental binary K_p data regression.

The procedure for evaluating binary isotherms according to the HT-CPM (Harlick & Tezel-Concentration Pulse Method) is generally performed by fitting the K_p vs. mole fraction (y_1) data to a function of i parameters:

$$K_p(\text{Experimental}) = f(\boldsymbol{A_i}, \boldsymbol{y_1}) \tag{4}$$

Provided this functional form fits the data well, the isotherm slope functions are derived from $f(\boldsymbol{A_i}, \boldsymbol{y_1})$ with unknown parameters, B_i and C_i, as follows:

$$\frac{dq_1}{dP_1} = \frac{df(\boldsymbol{A_i}, \boldsymbol{y_1})}{dy_1} = g(\boldsymbol{B_i}, \boldsymbol{y_1}) \tag{5}$$

$$\frac{dq_2}{dP_2} = \frac{df(\boldsymbol{A_i}, \boldsymbol{y_1})}{dy_1} = h(\boldsymbol{C_i}, \boldsymbol{y_1}) \tag{6}$$

The isotherms are found by the integration of Eqs. (5) and (6).

$$q_1 = \int g(\boldsymbol{B_i}, \boldsymbol{y_1})\, dP_1 \tag{7}$$

$$q_2 = \int h(\boldsymbol{C_i}, \boldsymbol{y_1})\, dP_2 \tag{8}$$

Note: $P_1 = P_{\text{Total}} y_1$, $P_2 = P_{\text{Total}}(1-y_1)$. When Eqs. (5) and (6) are substituted into Eq. (3), the following $\boldsymbol{K_p(B_i, C_i, y_1)}$ relationship is derived:

$$K_p(\text{Experimental}) = (1 - y_1)[g(\boldsymbol{B_i}, \boldsymbol{y_1})] + y_1[h(\boldsymbol{C_i}, \boldsymbol{y_1})] \tag{9}$$

The values of the B_i and C_i parameters are found by minimizing the following objective function:

$$\boldsymbol{SSR} = \sum_{y_1=y_{\min}}^{y_1=y_{\max}} \{K_p[\text{Experimental}] - ((1 - y_1)[g(\boldsymbol{B_i}, \boldsymbol{y_1})] + y_1[h(\boldsymbol{C_i}, \boldsymbol{y_1})])\}^2 \tag{10}$$

In our earlier paper (Harlick and Tezel, 2000) we have noted that the minimization of Eq. (10) could not be performed with only the data, since a number of solutions would exist. The following constraints were imposed on the system, in order to ensure that the solution reflects what is physically occurring:

(1) The end-points of the binary isotherms must coincide with the pure isotherms:

$$q_1(\text{Binary})|_{y_1=1} = q_1(\text{Pure})|_{P_{\text{Total}}} \tag{11}$$

$$q_2(\text{Binary})|_{y_1=0} = q_2(\text{Pure})|_{P_{\text{Total}}} \tag{12}$$

(2) If the adsorbates are similar in properties, especially at low surface coverage (θ), the isotherm slopes must also be set greater than or equal to zero across the entire range of y_1 (i.e. no maximum should be exhibited by the isotherms) (Calleja et al., 1998):

$$\frac{dq_1}{dP_1} \geq 0 \quad \text{and} \quad \frac{dq_2}{dP_2} \geq 0 \tag{13}$$

(3) The K_p function should pass through the experimental binary K_p data at $y_1 = 0$ and $y_1 = y_1(\max)$, this will ensure that function is well behaved as the experimental K_p data approach low ($y_1 \to 1$) or high values ($y_1 = 0$).

$$K_P(\text{Experimental})|_{y_1=0} = K_P[\text{RHS(Eq. (9))}]|_{y_1=0} \tag{14}$$

$$K_P(\text{Experimental})|_{y_1\to 1} = K_P[\text{RHS(Eq. (9))}]|_{y_1\to 1} \tag{15}$$

By using these constraints (Eqs. (11)–(15)) to bind the objective function (Eq. (10)) a constrained nonlinear regression is performed to determine the B_i and C_i parameters and thus determine the binary isotherms. The regressed K_p curve is given by Eq. (9) and the binary isotherms are given by Eqs. (7) and (8). The applicability of the HT-CPM has been shown with CO_2-N_2, CO_2-CH_4, and CH_4-N_2 binary adsorption systems using H-ZSM-5 with SiO_2/Al_2O_3 ratios of 30 and 280, (Harlick and Tezel, 2001, 2002) where other methods were not capable of producing feasible results (Harlick and Tezel, 2000).

In this study, the 5-parameter function that was proposed in our previous work (2001, 2002) was used

which is defined as follows:

$$K_p = A_1 + A_2 y_1 + A_3 y_1^2 + A_4 \ln(|y_1 + \lambda|) \quad \text{where } \lambda \neq 0 \tag{16}$$

The corresponding isotherm slope functions are:

$$\frac{dq_1}{dP_1} = g(B_i, y_1) = B_1 + 2B_2 y_1 + \frac{B_3}{(|y_1 + \lambda|)} \tag{17}$$

$$\frac{dq_2}{dP_2} = h(C_i, y_1) = C_1 + 2C_2 y_1 + \frac{C_3}{(|y_1 + \lambda|)} \tag{18}$$

Integration of Eqs. (17) and (18) gives following binary isotherm equations:

$$q_1 = \left\{ B_1 y_1 + B_2 y_1^2 + B_3 \ln\left(\left| \frac{y_1 + \lambda}{\lambda} \right| \right) \right\} P \tag{19}$$

$$q_2 = \left\{ C_1(1 - y_1) + C_2\left(1 - y_1^2\right) - C_3 \ln\left(\left| \frac{y_1 + \lambda}{1 + \lambda} \right| \right) \right\} P \tag{20}$$

When Eqs. (17) and (18) are substituted into Eq. (9), following equation is obtained:

$$K_p(\text{Experimental}) = (1 - y_1)\left[B_1 + 2B_2 y_1 + \frac{B_3}{(|y_1 + \lambda|)} \right] + y_1\left[C_1 + 2C_2 y_1 + \frac{C_3}{(|y_1 + \lambda|)} \right] \tag{21}$$

This equation is then used to define the objective function as follows:

$$\boldsymbol{SSR} = \sum_{y_1 = y_{\min}}^{y_1 = y_{\max}} \left\{ K_p(\text{Experimental}) - \left(\begin{array}{l} (1 - y_1)\left[B_1 + 2B_2 y_1 + \dfrac{B_3}{(|y_1 + \lambda|)} \right] \\ \quad + y_1\left[C_1 + 2C_2 y_1 + \dfrac{C_3}{(|y_1 + \lambda|)} \right] \end{array} \right) \right\}^2 \tag{22}$$

This objective function is minimized within the bounds of the constraints given by Eqs. (11)–(15) to determine the unknown B_i and C_i parameters. These parameters are then used in Eqs. (19) and (20) for the calculation of the binary isotherms and in Eq. (21) for the regressed K_p curve.

In order to reduce the binary data given in the literature, the component binary isotherms were fit to a smooth functional form, which best resembled the data, and the component slopes were determined. Each component slope was then substituted into Eq. (3), which defined the dimensional K_p data. This data was then treated as experimental data and each of the CPM data reduction techniques were applied and compared.

Numerical Methods

In order to determine the parameters for the binary adsorption data (given in the literature) to an appropriate functional form, a non-linear regression was performed using a modified Levenberg-Marquardt algorithm with a finite difference Jacobian. To find the solution to the VV-CPM and TT-CPM approaches, the same non-linear regression technique was used to determine the A_i parameters, and a matrix based solution procedure was used to determine the B_i and C_i. To find the optimal values of the B_i and C_i parameters for the HT-CPM (Eq. (22)) a non-linear constrained optimization technique was used. This was based on a Generalized Reduced Gradient (GRG2) nonlinear optimization code. Quadratic extrapolation was employed to obtain initial estimates of the basic variables in each one-dimensional search. The Jacobian for the objective and constraint functions were approximated by a central finite difference approach. A quasi-Newton iteration method was also used. Tolerance and convergence were each set at 10^{-6}. The solution was taken when no further change in Eq. (22) could be obtained for a wide range of starting values. This wide range of initial guesses ensured that the absolute and not the local minimum was obtained for each system.

Results

In order to evaluate the ability of the data reduction techniques used for determining binary adsorption isotherms from the concentration pulse method, several statically determined binary systems from the literature were chosen and studied. Several static data were chosen so that the effective binary K_p data would vary from linear to non-linear responses. By using these

static binary isotherms, the slopes were determined and applied to Eq. (3) in order to determine the effective binary response that would be obtained with the CPM. For each system, points were acquired at the same locations as the static binary data. By using these points, regressions were performed for each CPM approach, and the binary isotherms were determined. These binary isotherms obtained with different CPM methods were compared to the original statically determined data.

CH_4-CO_2 Activated Carbon

The first system examined was CH_4-CO_2 with BPL Activated Carbon (Golden and Sircar, 1994) and is shown in Fig. 1. The points represent the static data, and the curves represent a functional fit of the data. The regression of the static data was performed so that the first derivative could be obtained. Under this regression, the data was assumed smooth and continuous along the path of the static data. Using the resulting functions' first derivatives, the overall binary co-efficient (K_p) was determined, according to Eq. (3). This binary adsorption data set was chosen since adsorbates behaved linearly and K_p values did not change much.

Various CPM approaches were applied to the generated K_p data. The results of the binary K_p regressions

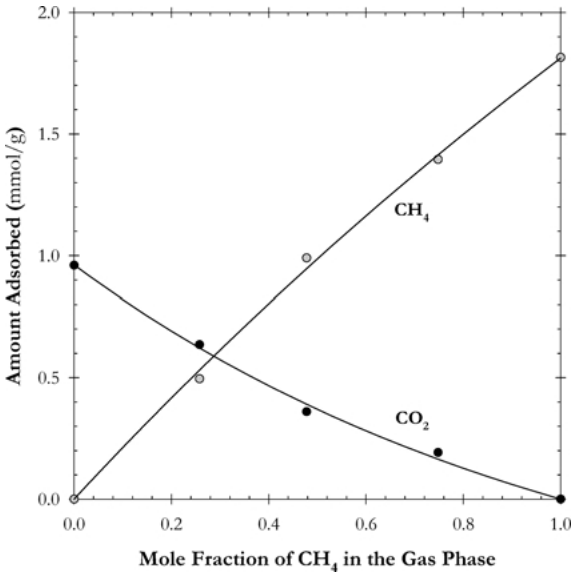

Figure 1. Statically determined CH_4-CO_2 binary isotherms with BPL AC (Golden and Sircar, 1994). Symbols represent the static data, and the curves represent the data regressions.

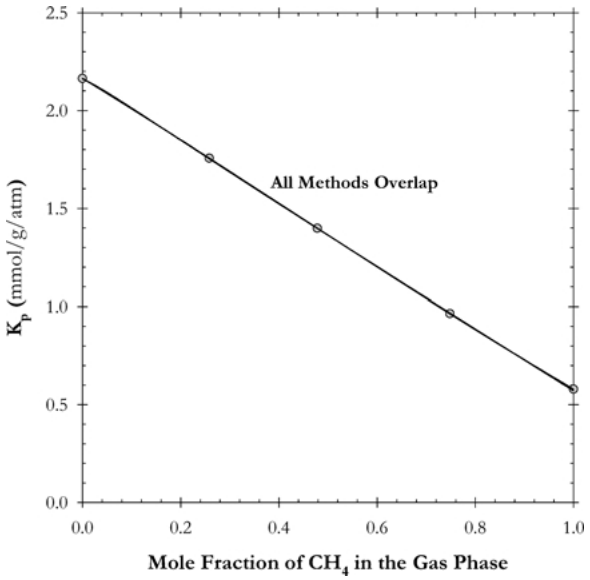

Figure 2. Binary K_p data reduced from the statically determined binary isotherms for CH_4-CO_2 with BPL AC. The symbols represent the statically reduced data, and the curves represent the VV-CPM, TT-CPM and HT-CPM approaches for data reduction.

using various expressions stated by each CPM approach are shown in Fig. 2, where the points represent the static data locations. For this binary system, all of the regressions provided similar results, and therefore appear to overlap each other in Fig. 2. Since the binary K_p data followed a near linear trend with increasing CH_4 pressure, each of the functions were able to fit the data well.

The resulting binary isotherms provided by each of the CPM approaches are shown in Fig. 3, where the static data are represented as symbols. As shown in Fig. 3, all of the CPM approaches produced the same set of binary isotherms, further; these isotherms also reproduced the same set given by the statically determined data (Golden and Sircar, 1994). The results show that all of the CPM data reduction approaches are capable of reducing linear binary K_p data to the original binary isotherm forms obtained from statically determined data. When K_p data behaves linearly, it does not matter which CPM data reduction approach is used for the determination of the binary isotherms.

CO_2-C_2H_4 13X

The next system examined was CO_2-$C_2H_4$with 13X (Hyun and Danner, 1982) and is shown in Fig. 4. The

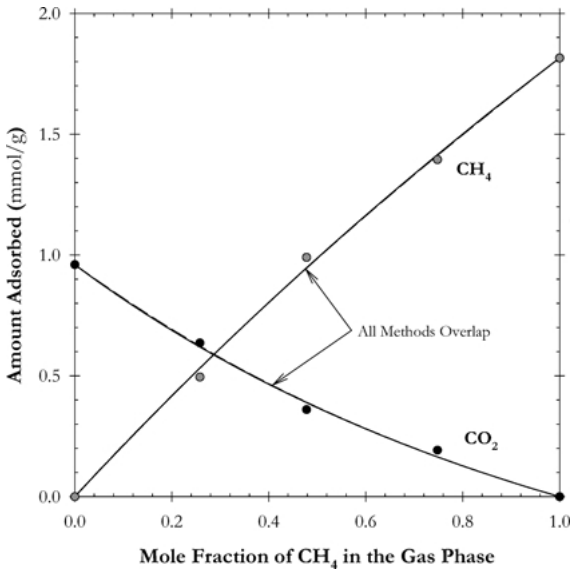

Figure 3. Binary isotherms determined by the VV-CPM, TT-CPM and HT-CPM data reduction techniques applied to the binary K_p defined from the statically determined isotherms for CH_4-CO_2 with BPL AC. The symbols represent the static data, and the curves represent the VV-CPM, TT-CPM and HT-CPM.

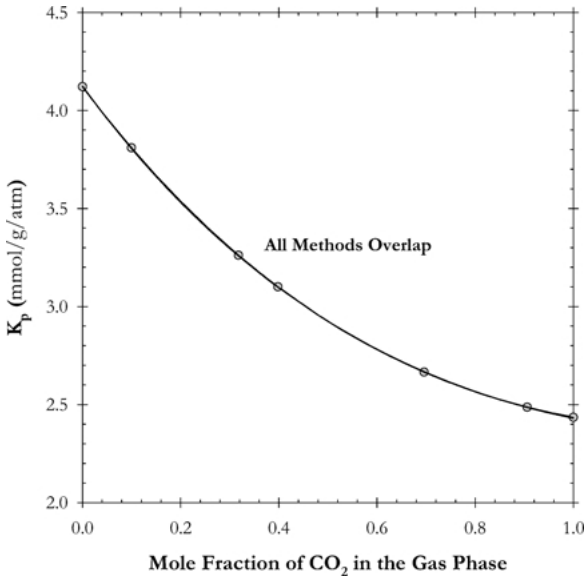

Figure 5. Binary K_p data reduced from the statically determined binary isotherms for CO_2-C_2H_4 with 13X. The symbols represent the statically reduced data, and the curves represent the VV-CPM, TT-CPM and HT-CPM approaches for data reduction.

points represent the static data, and the curves represent a functional fit of the data. This data set was chosen to illustrate binary K_p data that exhibit a slight degree of concavity (in the direction of the origin) with values of K_p not changing much. The same procedure was applied as stated with the CH_4-CO_2 system previously mentioned, and the results are shown in Fig. 4.

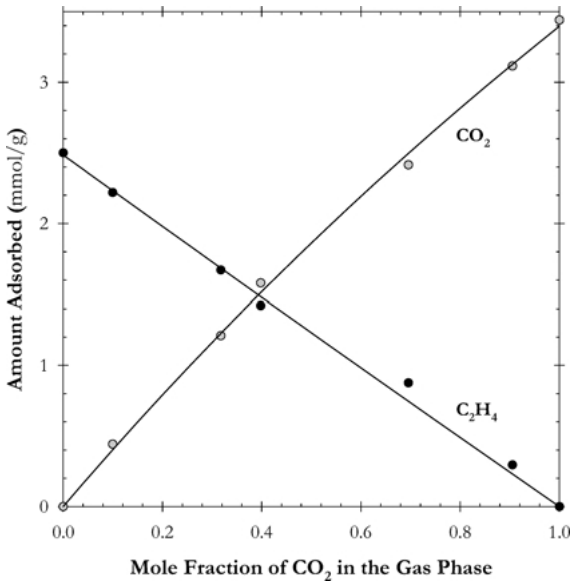

Figure 4. Statically determined CO_2-C_2H_4 binary isotherms with 13X (Hyun and Danner, 1982). Symbols represent the static data, and the curves represent the data regressions.

Various CPM approaches were applied to the generated K_p data. The results of the binary K_p regressions using the various expressions stated by each CPM approach are shown in Fig. 5, where the points represent the static data locations. For this binary system, all of the regressions provided similar results, and therefore appear to overlap each other in Fig. 5. Since the binary K_p data followed a polynomial trend with changing CO_2 pressure, all of the functions were able to fit the data well.

The resulting binary isotherms provided by each of the CPM approaches are shown in Fig. 6 and compared to the original static data that are represented as symbols. For this system, the VV-CPM method is at its limit as can be seen from this figure. Although the binary K_p data fit for this method is good (Fig. 5), it introduced curvature to the binary isotherms by overpredicting the original statically determined binary data. As shown in Fig. 6, TT-CPM and HT-CPM approaches produced exactly the same set of binary isotherms. They both reproduced the original data set given by the statically determined data (Hyun and Danner, 1982). These results show that the TT-CPM and HT-CPM data

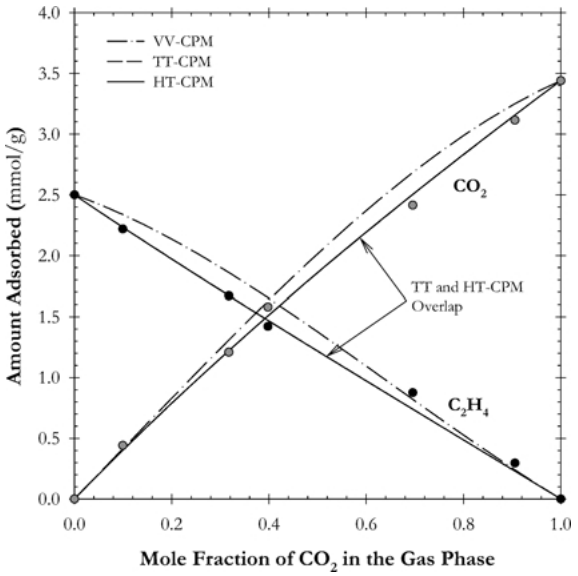

Figure 6. Binary isotherms determined by the VV-CPM, TT-CPM and HT-CPM data reduction techniques applied to the binary K_p defined from the statically determined isotherms for CO_2-C_2H_4 with 13X. The symbols represent the static data, and the curves represent the VV-CPM, TT-CPM and HT-CPM.

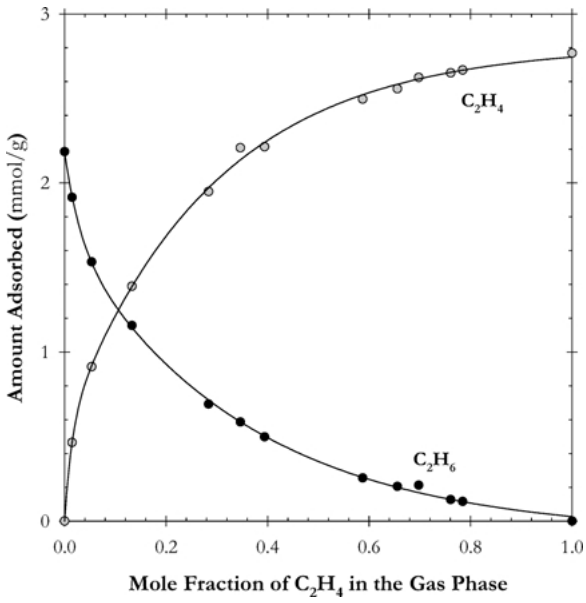

Figure 7. Statically determined C_2H_4-C_2H_6 binary isotherms with 13X (Danner and Choi, 1978; Hyun and Danner, 1982). Symbols represent the static data, and the curves represent the data regressions.

reduction approaches are capable of reducing slightly concave binary K_p data to the same binary isotherm forms obtained from statically determined data. However, while the VV-CPM approach was well behaved for the K_p data curve fit, it can not be relied on to produce results, which coincide with statically determined binary isotherms. Therefore, the VV-CPM approach should only be applied to binary systems where the binary K_p response is linear.

C_2H_4–C_2H_6 13X

The binary data that has been examined and re-examined often in the literature is the C_2H_4-C_2H_6 system with 13X (Danner and Choi, 1978 [static]; Hyun and Danner, 1982 [chromatographic]; Buffman et al., 1999 [data reduction]). This data set was chosen, since the K_p data varied over an order of magnitude. For this system, the data given by Danner and Choi (1978) was used as the static data and the data given by Hyun and Danner (1982) was used as the binary K_p data. Therefore, there was no need for the initial regression of the binary isotherms. However, since both static and chromatographic data were available for this system, a comparison of the chromatographic binary K_p data and the K_p data obtained by regression of the static data was performed. The static data and regressions are given in Fig. 7. From the static data (symbols) shown in Fig. 7, it can be seen that both components exhibit non-linear behaviour, where ethylene is dominant. The curve fits (solid lines) of the data are also shown. The quality of each fit is excellent. Using these regressions, the static data was reduced to binary K_p data by using Eq. (3).

The comparison of the chromatographic binary K_p data from Hyun and Danner (1982) and the K_p data reduced from the static data (Danner and Choi, 1978) are given in Fig. 8. The data show that the assumption of using reduced static data in place of chromatographically determined binary K_p data is justified. The only discrepancy between the data is when the mole fraction of ethylene is below 0.30, and a slight offset at high mole fractions. However, since the scale is semi-log, the discrepancy at high mole fractions is negligible. Although the two sets of data shown in Fig. 8 are relatively equal, the reasoning for the discrepancy may be related to the assumptions applied to the chromatographic method, or to the general experimental procedures involved with both the static and chromatographic methods. One possible reason for the difference may lie with the size of the injected sample used by Hyun and Danner (1982) with the CPM. As stated previously, the size of the injection must be small enough so that the point at

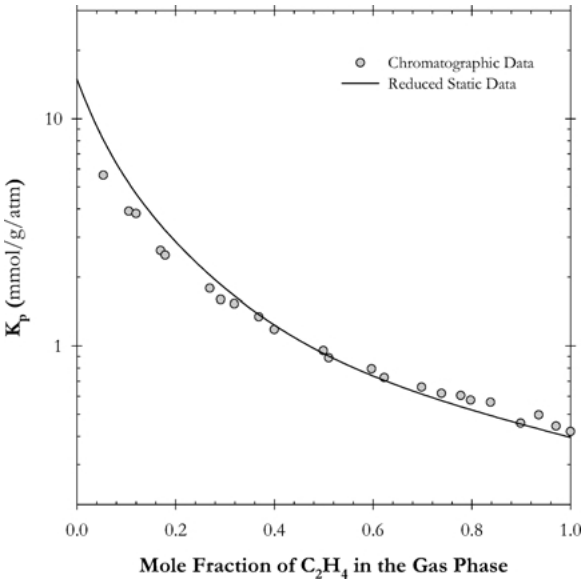

Figure 8. Comparison of the binary K_p data reduced from the statically determined binary isotherms for C_2H_4-C_2H_6 with 13X and the binary K_p data obtained with the CPM as reported by Hyun and Danner (1982).

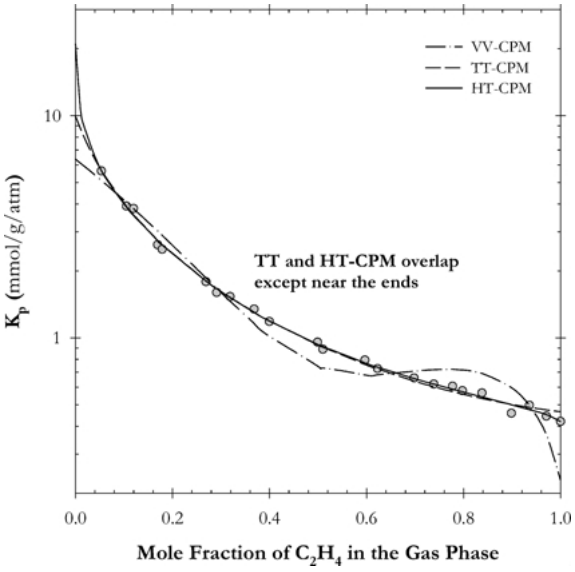

Figure 9. Binary K_p data given by Hyun and Danner (1982) for C_2H_4-C_2H_6 with 13X using the CPM. The curves represent the VV-CPM, TT-CPM and HT-CPM approaches for data reduction.

which the system perturbation occurs does not shift. If the sample size is too large, the assumption of pressure and density will not hold, and the local gas phase concentration will shift to a higher quantity (Buffman et al., 1999).

The first step of each of the CPM's is to perform the regression of the binary K_p data to the stated function. These results are shown in Fig. 9, where the points represent the chromatographic data and the curves represent each of the regressions for each of the CPM approaches (VV-CPM, TT-CPM, and HT-CPM). From this figure, it can be seen that the polynomial function used with the VV-CPM does not fit the data at all, and is therefore not used in any further calculations. The functions provided with the TT-CPM and HT-CPM both fit the experimental data well. The only difference is that the function used with the TT-CPM method does exhibit a slight deviation from the experimental data close to pure C_2H_4 concentration in the gas phase. The HT-CPM procedure does not fit an unrestricted function to the data; rather a constrained regression is applied. The effect of the constraints can be seen as the experimental data points at the extremes of the experimental data coincide with the regressed curve.

The binary isotherms obtained with the TT-CPM and HT-CPM approaches are shown in Fig. 10. The effect of the data reduction technique can be shown from this figure. The HT-CPM approach produced results that were closer to the static data than the TT-CPM approach. The reason for the difference may be caused by the

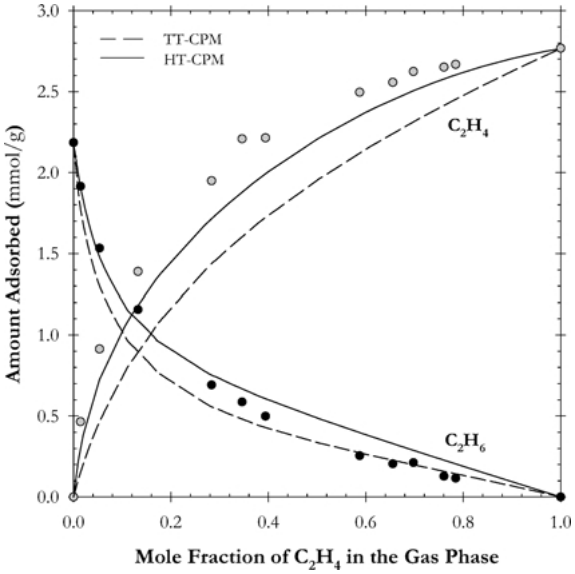

Figure 10. Binary isotherms determined by the TT-CPM and HT-CPM data reduction techniques applied to the binary K_p given by Hyun and Danner (1982) for C_2H_4-C_2H_6 with 13X using the CPM. The symbols represent the static data, and the curves represent the TT-CPM and HT-CPM.

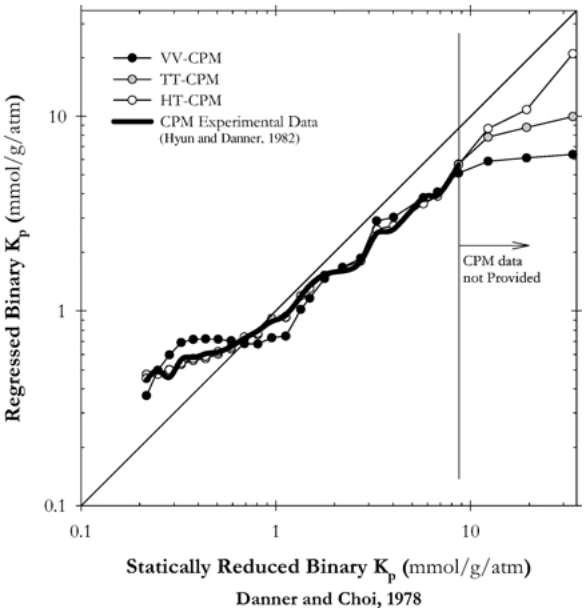

Figure 11. Comparison of the binary K_p data regressions for the TT-CPM and HT-CPM (using the CPM data provided by Hyun and Danner (1982)) and the statically reduced binary K_p data. The TT-CPM and HT-CPM were performed on the CPM data and therefore no data was available beyond the labeled vertical line.

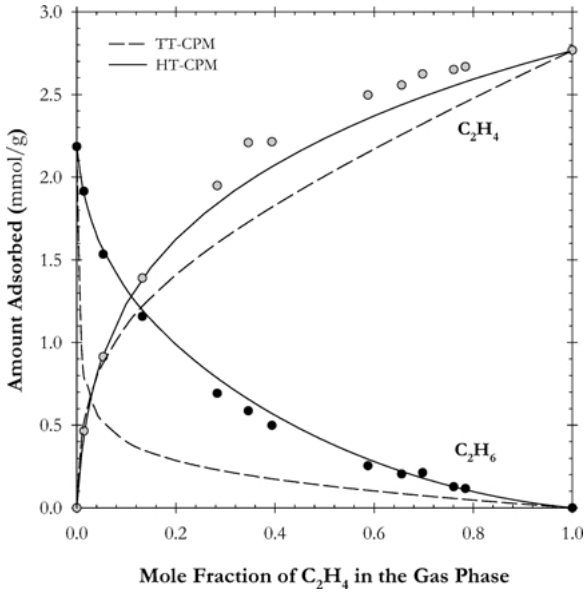

Figure 12. Binary isotherms determined by the TT-CPM and HT-CPM data reduction techniques applied to the binary K_p data reduced from the static data provided by Danner and Choi (1978) for C_2H_4-C_2H_6 with 13X. The symbols represent the static data, and the curves represent the TT-CPM and HT-CPM.

quality of the regression and the approach for the data reduction. The data reduction technique employed with the HT-CPM is a constrained regression where the end-points are fixed. For this system, the data point at $y_1 = 0$ was not available from the chromatographic data given by Hyun and Danner (1982). Therefore, the next point was applied as an end point and used as a constraint. It is important to note that the HT-CPM did provide data as $y_1 \rightarrow 1$ that resembled the data obtained by reducing the static data. The TT-CPM does not require any constraints and thus the data was lower than the statically reduced data. The discrepancy between TT-CPM, HT-CPM and statically reduced K_p data is shown in Fig. 11.

In order to check the applicability of the TT-CPM and HT-CPM methods further, isotherms were produced based on the statically reduced binary K_p data shown in Fig. 8 and are given in Fig. 12. The results of the HT-CPM approach exhibited some improvement; however, the TT-CPM approach produced results with even larger deviations, when compared to the statically determined binary isotherms. Therefore, by comparing the two sets of CPM reduced binary isotherms, it can be concluded that the TT-CPM approach should be used with binary K_p data that do not exhibit a large degree concavity. However, further investigation into this point needs to be conducted.

CO-O_2 5A

The last system investigated was CO-O_2 with 5A (Sircar, 1991; Danner and Wenzel, 1969). This system was chosen to represent the extreme case of non-linear binary K_p behavior with several orders of magnitude change in K_p values. The statically determined data are shown in Fig. 13 as symbols and the regression of the data are represented as curves. Once again, the data was assumed smooth and continuous along the path of the static data. Using the resulting functions' first derivatives, the overall binary co-efficient, K_p, was determined, according to Eq. (3).

From the generated K_p data, the various CPM approaches were applied. The results of the binary K_p regressions using the various expressions stated by each CPM approach are shown in Fig. 14, where the points represent the static data locations. For this binary system, the VV-CPM approach was not considered since the applicability of this approach has already proven to be invalid for highly non-linear systems. Therefore,

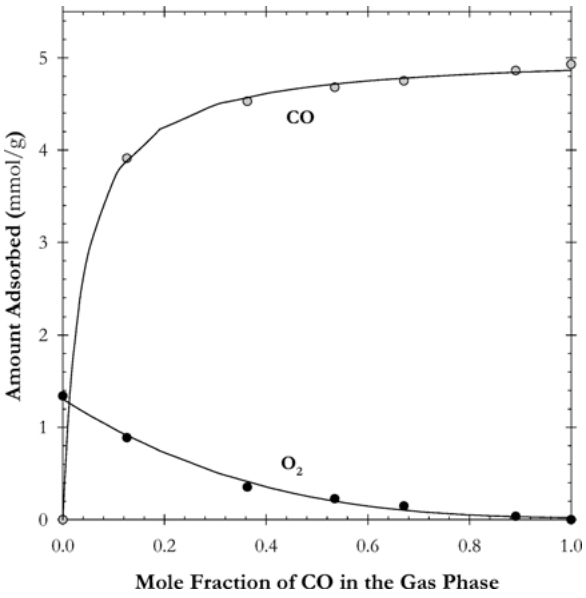

Figure 13. Statically determined CO-O_2 binary isotherms with 5A (Sircar, 1991; Danner and Wenzel, 1969). Symbols represent the static data, and the curves represent the data regressions.

only the TT-CPM and HT-CPM approaches were applied. As shown in Fig. 14, the regression of the binary K_p data was well described by the HT-CPM approach. The TT-CPM approach also described the

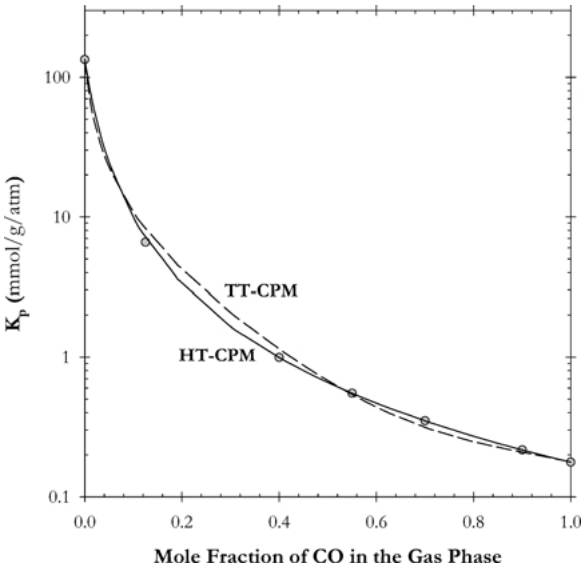

Figure 14. Binary K_p data reduced from the statically determined binary isotherms for CO-O_2 with 5A. The symbols represent the statically reduced data, and the curves represent the TT-CPM and HT-CPM approaches for data reduction.

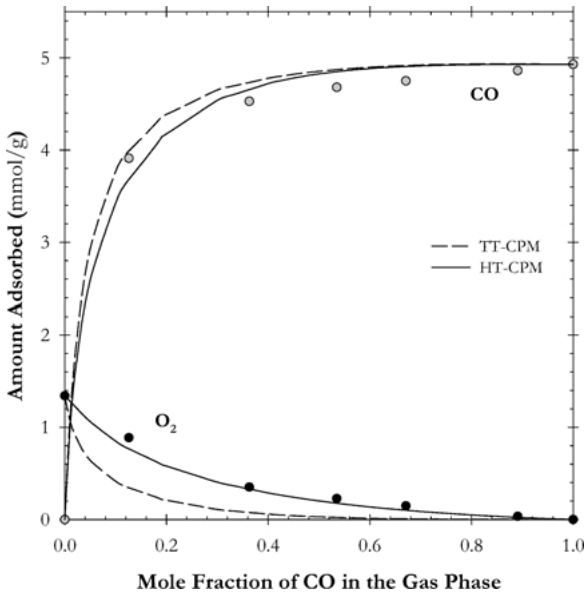

Figure 15. Binary isotherms determined by the VV-CPM, TT-CPM and HT-CPM data reduction techniques applied to the binary K_p defined from the statically determined isotherms for CO-O_2 with 5A. The symbols represent the static data, and the curves represent the TT-CPM and HT-CPM.

statically reduced data; however, positive deviations were present in the range of $0.15 \leq y_1 \leq 0.45$ and small negative deviations were observed in the range of $0.55 \leq y_1 \leq 0.90$. The effect of the positive deviation is that the magnitude of the binary K_p data is greater, and thus will allow for higher adsorption capacities, whereas lower capacities would be realized with negative deviations.

The resulting binary isotherms are given in Fig. 15 as curves and the statically determined binary isotherms as points. From these data, it can be concluded that both CPM approaches reproduce the selectively adsorbed component (CO in this case) isotherm well. However, the less adsorbed component isotherm is not described correctly by the TT-CPM approach. These results follow the same trend noted with the C_2H_4-C_2H_6 binary system with 13X. Therefore, it can be concluded that the TT-CPM approach should not be applied to highly non-linear binary K_p data.

Conclusions

The applicability of the concentration pulse method for determining binary adsorption isotherms has been examined. The applicability of the VV-CPM, TT-CPM

and HT-CPM approaches to the binary K_p data reduction has been compared to statically determined binary isotherms. The results indicate that the CPM will provide binary isothems that are similar to those obtained by static methods. However, the data reduction technique will influence the binary adsorption results. In this study, it was concluded that the VV-CPM approach was applicable to linear binary K_p data, only. Shah (1988) also concluded that this was the case. The TT-CPM was found to have applicability to linear and slightly non-linear binary K_p data. The HT-CPM approach was found to have applicability to all the binary adsorption systems used in this work, which represented different possible behavior of K_p data. Therefore, HT-CPM is the most versatile approach to use for determining binary isotherms experimentally using CPM.

Nomenclature

A, B, C	Parameters (mmol/g/atm)
c	Concentration measured as voltage (mv)
f, g, h	Function
K	Effective isotherm slope (Dimensionless)
K_P	Effective isotherm slope (mmol/g/atm)
L	Length of the column (m)
P	Pressure (atm)
q	Amount adsorbed (mmol/g)
t	Time (sec)
x	Mole fraction in the adsorbed phase (Dimensionless)
y	Mole fraction in the gas phase (Dimensionless)

Greek Letters

å	Bed porosity (Dimensionless)
è	Fractional coverage (Dimensionless)
ë	Parameter in Eq. (16) (Dimensionless)
ì	Mean retention time (sec)
í	Interstitial velocity (cm/sec)
ρ	Density (g/cc)

Subscripts

1	Component 1
2	Component 2
i	Index
Max	Maximum
Min	Minimum
p	Pellet

Abbreviations

CPM	Concentration Pulse Method
GC	Gas Chromatograph
HT-CPM	Harlick and Tezel—Concentration Pulse Method
LHS	Left Hand Side
MFC	Mass Flow Controller
RHS	Right Hand Side
SSR	Sum of Square Residuals
TCD	Thermal Conductivity Detector
TT-CPM	Triebe and Tezel—Concentration Pulse Method
VV-CPM	Van der Vlist and Van der Meijden—Concentration Pulse Method

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