Short report

Ideal adsorbed solution theory solved with direct search minimisation

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ABSTRACT

The ideal adsorbed solution theory (IAST) is the most widespread theory for multicomponent adsorption interpretation. It postulates the existence of an adsorbed phase which behaves as a Raoult ideal solution. The theory results in a system of nonlinear algebraic equations which are solved to know the composition of the adsorbed mixture at equilibrium. In this paper an investigation on an alternative method for the IAST equations solution is proposed which is based on the minimisation of an objective function representing the iso-spreading pressure condition. This approach to the solution of the IAST equations reduces in some cases the computational effort and mitigates the issues of the currently adopted approaches (inversion of functions and initial guess). For binary systems, direct search minimisation approach is faster than the classic IAST equations solution approach up to 19.0 (Dual Langmuir isotherm) and 22.7 times (Toth isotherm). In ternary systems, this difference decreases to 10.4 (O'Brien and Myers isotherm) times. Compared to FASTIAS approach, direct search minimisation is up to 4.2 times slower in ternary systems.

1. Introduction

Adsorption materials are increasingly attracting interest because they permit almost selectively the separation of targeted compounds, often reducing energy consumption compared with traditional separation techniques. Thanks to their ability of selectively capturing single compounds from complex multicomponent mixtures (Minceva and Rodrigues, 2005) and the suitability of triggering the heat using a concentration swing (Yu et al., 2013), new adsorptive technologies are currently commercialised (Dawoud et al., 2012; Ramaswamy et al., 2013; Santori et al., 2013) or at R&D stage (Liu et al., 2011; Santori et al., 2014). In all cases, adsorption thermodynamics plays a fundamental role in the system design.

In the majority of practical cases, the separation of a selected compound from a multicomponent mixtures is required and consequently multicomponent adsorption thermodynamic theories are regarded with a particular interest. Presently, the most widespread multicomponent adsorption theory is the ideal adsorbed solution theory (IAST) (Myers and Prausnitz, 1965). The reason of its success consists in the possibility to predict multicomponent adsorption equilibrium from single component adsorption isotherms.

In the IAST, an ideal gas phase and an adsorbed phase are in equilibrium. The adsorbed phase is considered an ideal solution following the Raoult's law. In several cases this is an acceptable assumption or can offer a useful initial result for a more refined interpretation (Cessford et al., 2012; Yun et al., 2002).

Multicomponent gaseous mixtures are considered in this paper, but the IAST can be applied similarly to liquid mixtures. The mathematical formulation of the problem consists in the solution of the following algebraic-integral equations:

$$P_{tot}y_i = P_i^0 x_i \quad i = 1, 2, ...NC \tag{1}$$

$$\sum_i^{NC} x_i = 1 \tag{2}$$

$$n_i = f_i(P_i^0, T) \quad i = 1, 2, ...NC \tag{3}$$

$$\frac{\pi_i A}{RT} = \int_0^{P_i^0} n_i d(\ln(P_i^0)) \quad i = 1, 2, ...NC \tag{4}$$

where P_{tot} [kPa] is the total pressure of the gaseous mixture flowing on the adsorbent surface, y_i is the molar fraction of the component i of the non-adsorbed mixture, x_i is the molar fraction of the component i in the adsorbed phase, NC is the total number of components, n_i [mol/kg] is the adsorption amount of component i from the adsorption isotherm, P_i^0 [kPa] is the surface pressure of the component i, T [K] is the equilibrium temperature, π_i [kPa m] is the specific spreading pressure of the component i, A [m^2/kg] is the specific surface area covered by the adsorbed mixture. For the solution of the Eqs. (1)–(4) the condition of thermodynamic equilibrium

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must be considered. The system is at equilibrium when the reduced spreading pressure ($\pi_i A/(RT)$) has the same value for each component. So the equilibrium condition is represented by the following iso-spreading pressure condition:

$$\frac{\pi_i A}{RT} = \text{constant} \quad i = 1, 2, \ldots\ldots NC \tag{5}$$

The problem can be solved giving P_{tot}, y_i and the adsorption isotherms ($f_i(P_i^0, T)$ with parameters computed by single component adsorption equilibrium data. The unknowns of the system are x_i, π_i, P_i^0 and q_i^0.

An extensive review of the different approaches proposed for the solution of the problem above has been presented in [8], highlighting the following main issues of the described strategies:

1) An inversion of the spreading pressure function is needed and only in few cases such inversion is analytical;
2) An initial guess should be provided in order to find a solution.

These issues are overcome following the method proposed in (Rubiera Landa et al., 2013). The only claimed limit of the procedure in (Rubiera Landa et al., 2013) consists in the computational load, which is comparable with the classical solution approaches (Do, 1998; Myers and Valenzuela, 1986; Valenzuela and Myers, 1989), making the method (FASTIAS) presented in (O'Brien and Myers, 1985) and successively refined in (O'Brien and Myers, 1988) still the quickest numerical method for the solution of IAST equations.

In some cases explicit solution of the IAST equations can be formulated for binary systems. In (LeVan and Vermeulen, 1981) a method is presented for deriving explicit binary isotherms from simple single isotherm (Langmuir and Freundlich) in form of series expansions.

Assuming single isotherms fitted considering equal saturation capacities, binary adsorption isotherms have been derived for Brunauer-Emmet-Teller (BET)-Langmuir, BET-BET, Langmuir-Langmuir, anti-Langmuir-anti-Langmuir and quadratic-quadratic (Gritti and Guiochon, 2003a, 2003b; Tarafder and Mazzotti, 2012). In addition, explicit isotherms have been derived also without the previous assumption (Frey and Rodrigues, 1994; Ilic et al., 2010).

Integration of IAST equations with adsorptive bed dynamics equations is an additional issue. There are three possibilities to couple IAST equations in adsorptive bed dynamics. Firstly, the spreading pressure can be treated as a dependent variable of time and space and added to the differential system describing bed dynamics (Mota and Rodrigo, 2000). This results in a strongly nonlinear system of differential-algebraic equations which is difficult to solve, computationally expensive and time consuming. For this reason the most common methodology consists on the computation of the adsorption equilibrium separately to bed dynamics in each time step. Also the approach is time consuming because it obliges to exit and enter continuously the IAST equations solver with new conditions. The third strategy is the use of the B-Spline approach (Santos et al., 2011). It allows to pre-compute the equilibrium states and this can mitigate the issues for the binary system case, but for more than two components the B-Spline approach results in additional multidimensional fitting issues, losing its advantages.

This paper presents an investigation on the solution of the IAST equations using analytical expression of the spreading pressures for the adsorbed components and a direct search minimisation approach for the iso-spreading pressure condition of Eq. (5). The method is tested on a number of adsorption isotherms and on binary and ternary systems.

The immediate way to implement direct search methods for adsorptive bed dynamics is the use of a separate solver. The proposed investigation is not a contribution to the solution of these issues, which are still open.

On the basis of the reported results, direct search methods are expected to reduce the time spent for equilibrium calculations in comparison with the traditional IAST method and consequently the overall bed dynamics simulation times.

2. Solution of the IAST equations through direct search minimisation methods

The IAST equation system can be reduced through successive substitution of variables to a smaller system of iso-spreading pressure conditions. Table 1 shows the analytically integrated form of the spreading pressure for some adsorption isotherms. The spreading pressure are expressed in terms of molar fractions x_i through a preliminary change of variable from P_i^0 to x_i substituting the Eq. (1)–(4).

For sake of clarity, taking the Dual Langmuir isotherm, spreading pressure in terms of molar fraction is obtained by the following change of variable:

$$d\ln\left(\frac{P_{tot}y_i}{x_i}\right) = -\frac{1}{x_i}dx_i \tag{6}$$

Accordingly, the spreading pressure integral becomes:

$$\frac{\pi_i A}{RT} = \int -\left(\frac{q_{s1,i}b_{1,i}\left(\frac{P_{tot}y_i}{x_i}\right)}{x_i + x_i b_{1,i}\left(\frac{P_{tot}y_i}{x_i}\right)} + \frac{q_{s2,i}b_{2,i}\left(\frac{P_{tot}y_i}{x_i}\right)}{x_i + x_i b_{2,i}\left(\frac{P_{tot}y_i}{x_i}\right)}\right)dx_i$$

$$= \int \left(-\frac{q_{s1,i} + q_{s2,i}}{x_i} + \frac{q_{s1,i}}{x_i + P_{tot}y_i b_{1,i}} + \frac{q_{s2,i}}{x_i + P_{tot}y_i b_{2,i}}\right)dx_i \tag{7}$$

The integration of Eq. (7) results in the expression listed in Table 1 for Dual Langmuir isotherm. An additional result of this paper is represented by the analytical expression for spreading pressure of the Unilan isotherm, which was deemed not computable (Do, 1998).

Using the spreading pressures listed in Table 1, the iso-spreading pressure condition can be set as a minimisation problem. Using