



THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

Ideal adsorbed solution theory solved with direct search minimisation

Citation for published version:

Santori, G, Luberti, M & Ahn, H 2014, 'Ideal adsorbed solution theory solved with direct search minimisation' Computers and Chemical Engineering, vol. 71, pp. 235-240. DOI: 10.1016/j.compchemeng.2014.07.027

Digital Object Identifier (DOI):

[10.1016/j.compchemeng.2014.07.027](https://doi.org/10.1016/j.compchemeng.2014.07.027)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Early version, also known as pre-print

Published In:

Computers and Chemical Engineering

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.



1 Published in: Computers and Chemical Engineering (2014) 71:235

3 Ideal adsorbed solution theory solved with direct search minimisation

4 Giulio Santori^{a*}, Mauro Luberti^a, Hyungwoong Ahn^a

6 *corresponding author: Dr. Giulio Santori, g.santori@ed.ac.uk, tel: +4401316519043, fax: +4401316506551

7 ^a The University of Edinburgh, School of Engineering, Institute for Materials and Processes, Sanderson
8 Building, The King's Buildings, Mayfield Road, EH9 3JL, Edinburgh, Scotland, UK

10 Abstract

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

23 Keywords: *ideal adsorbed solution theory; adsorption equilibria; adsorption thermodynamics; solution
24 algorithm;*

26 Introduction

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

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

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

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

$$45 P_{tot} y_i = P_i^0 x_i \quad i = 1, 2, \dots, NC \quad (1)$$

$$46 \sum_i^{NC} x_i = 1 \quad (2)$$

$$47 n_i = f_i(P_i^0, T) \quad i = 1, 2, \dots, NC \quad (3)$$

$$48 \frac{\pi_i A}{RT} = \int_0^{P_i^0} n_i d(\ln(P_i^0)) \quad i = 1, 2, \dots, NC \quad (4)$$

49 where P_{tot} [kPa] is the total pressure of the gaseous mixture flowing on the adsorbent surface, y_i is the molar
50 fraction of the component i of the non-adsorbed mixture, x_i is the molar fraction of the component i in the

51 adsorbed phase, NC is the total number of components, q_i^0 [mol/kg] is the specific adsorbed amount of the
 52 component i at equilibrium, P_i^0 [kPa] is the surface pressure of the component i , T [K] is the equilibrium
 53 temperature, π_i [kPa m] is the specific spreading pressure of the component i , A [m²/kg] is the specific
 54 surface area covered by the adsorbed mixture. For the solution of the eqns (1-4) the condition of
 55 thermodynamic equilibrium must be considered. The system is at equilibrium when the reduced spreading
 56 pressure ($\pi_i A / (RT)$) has the same value for each component. So the equilibrium condition is represented by
 57 the following iso-spreading pressure condition:

$$58 \quad \frac{\pi_i A}{RT} = \text{constant} \quad i = 1, 2, \dots, NC \quad (5)$$

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

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

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

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

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

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

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

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

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

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

99

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

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

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

$$107 \quad d \ln \left(\frac{P_{tot} y_i}{x_i} \right) = - \frac{1}{x_i} dx_i \quad (6)$$

108 Accordingly, the spreading pressure integral becomes:

$$109 \quad \frac{\pi_i A}{RT} = \int - \left(\frac{q_{s1,i} b_{1,i} \left(\frac{P_{tot} y_i}{x_i} \right)}{x_i + x_i b_{1,i} \left(\frac{P_{tot} y_i}{x_i} \right)} + \frac{q_{s2,i} b_{2,i} \left(\frac{P_{tot} y_i}{x_i} \right)}{x_i + x_i b_{2,i} \left(\frac{P_{tot} y_i}{x_i} \right)} \right) dx_i =$$

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

110 The integration of eq. (7) results in the expression listed in Table 1 for Dual Langmuir isotherm. An
 111 additional result of this paper is represented by the analytical expression for spreading pressure of the Unilan
 112 isotherm, which was deemed not computable (Do, 1998).
 113
 114

Table1: List of the analytical expressions of the spreading pressure for different adsorption isotherms

	Isotherm	Reduced Spreading Pressure
Dual Langmuir	$q_i = q_{s1,i} \frac{b_{1,i} P}{1 + b_{1,i} P} + q_{s2,i} \frac{b_{2,i} P}{1 + b_{2,i} P}$	$\frac{\pi_i A}{RT} = -(q_{s1,i} + q_{s2,i}) \ln(x_i) + q_{s1,i} \ln(b_{1,i} y_i P_{tot} + x_i) + q_{s2,i} \ln(b_{2,i} y_i P_{tot} + x_i)$
Toth	$q_i = q_{s,i} \frac{b_i P}{[1 + (b_i P)^t]^{1/t}}$	$\frac{\pi_i A}{RT} = \frac{y_i P_{tot} b_i q_{s,i}}{x_i} {}_2F_1 \left(\frac{1}{t}; \frac{1}{t}; \left(1 + \frac{1}{t} \right); - \left(\frac{y_i P_{tot} b_i}{x_i} \right)^t \right)$ where ${}_2F_1$ is the Gauss hypergeometric function ${}_2F_1$
Unilan	$q_i = \frac{q_{s,i}}{2s_i} \ln \left(\frac{1 + b_i P e^{s_i}}{1 + b_i P e^{-s_i}} \right)$	$\frac{\pi_i A}{RT} = \frac{q_{s,i}}{2s_i} \left[\ln(x_i) \left(\ln \left(\frac{e^{s_i} (b_i y_i P_{tot} e^{s_i} + x_i)}{b_i y_i P_{tot} + e^{s_i} x_i} \right) - \ln \left(1 + \frac{e^{-s_i} x_i}{b_i y_i P_{tot}} \right) + \ln \left(1 + \frac{e^{s_i} x_i}{b_i y_i P_{tot}} \right) \right) - \dots \right]$ $\dots - Li_2 \left(- \frac{e^{-s_i} x_i}{b_i y_i P_{tot}} \right) + Li_2 \left(- \frac{e^{s_i} x_i}{b_i y_i P_{tot}} \right)$ where Li_2 is the dilogarithm function
O'Brien-Myers	$q_i = q_{s,i} \left[\frac{b_i P}{1 + b_i P} + \frac{\sigma_i^2 b_i P (1 - b_i P)}{2(1 + b_i P)^3} \right]$	$\frac{\pi_i A}{RT} = \frac{q_{s,i}}{2(b_i y_i P_{tot} + x_i)^2} \left(-b_i \sigma_i^2 y_i P_{tot} x_i + 2(b_i y_i P_{tot} + x_i)^2 \ln(x_i) - \dots \right)$ $\dots - 2(b_i y_i P_{tot} + x_i)^2 \ln(b_i y_i P_{tot} + x_i)$

115 Using the spreading pressures listed in Table 1, the iso-spreading pressure condition can be set as a
 116 minimisation problem. Using eq.(2), the objective function of the minimisation problem becomes for the
 117 binary case:
 118

$$119 \quad f_{binary}(x_1) = \left| \frac{\pi_1(x_1) A}{RT} - \frac{\pi_2(x_1) A}{RT} \right| \quad (8)$$

120 and for the ternary case:

$$121 \quad f_{ternary}(x_1, x_2) = \left(\left| \frac{\pi_1(x_1) A}{RT} - \frac{\pi_2(x_2) A}{RT} \right| + \left| \frac{\pi_1(x_1) A}{RT} - \frac{\pi_3(x_1, x_2) A}{RT} \right| \right) \quad (9)$$

122 Considering the isotherms in Table 1, the resulting objective functions present only a minimum whose
 123 coordinates correspond to the equilibrium condition. This feature makes the minimisation problem
 124 particularly easy to solve even by direct search local minimisation algorithms.

125 The advantage in the change of the independent variable of the spreading pressure (from P_i^0 to x_i) consists in
 126 the chance of constraining the molar fractions x_i in their feasible interval (0,1). So for the more general
 127 ternary case, the optimization problem is stated as:
 128

129 Minimize the objective function $f_{\text{ternary}}(x_1, x_2)$ subject to constraints $0 < x_1 < 1 - x_2$ and $0 < x_2 < 1 - x_1$

130

131

From the solutions of this problem the number of total adsorbed moles is calculated with:

132

$$\frac{1}{q_{\text{tot}}} = \sum_{i=1}^3 \left(\frac{x_i}{n_i (P_i^0)} \right) \quad (10)$$

133

All the computations presented in this paper were performed with Nelder-Mead minimisation algorithm (Nelder and Mead, 1965) operated with a working precision of 10^{-8} , which resulted in final residuals ranging between 10^{-7} and 10^{-9} . The residuals are far beneath the accuracy of the experimental values and coherent with the order of magnitude considered by other authors (O'Brien and Myers, 1985; O'Brien and Myers, 1998; Rubiera Landa et al, 2013). The comparisons presented in next sections aim to validate quantitatively the proposed approach.

139

3. Application to single equilibrium conditions

141

The minimisation approach is applied only to few case studies due to the limited number of experimental data for binary and ternary systems of acceptable quality. The parameters used for the single component adsorption isotherms are reported in Table 2 and Table 3.

144

Table 2: Parameters of the single component adsorption isotherms for the binary system Methane(1)/Ethane(2) on activated carbon BPL at 301.4 K (He et al., 2004)

	Pressure Range [kPa]	Dual Langmuir				Toth		t
		q_{s1}	b_1	q_{s2}	b_2	q_s	b	
Methane	0-3220.7	0.894481	$8.368828 \cdot 10^{-3}$	4.921966	$6.950138 \cdot 10^{-4}$	7.912945	$1.520872 \cdot 10^{-3}$	0.5620853
Ethane	0-791.98	4.698140	$5.876234 \cdot 10^{-3}$	1.173161	$1.683690 \cdot 10^{-1}$	9.382593	$4.406557 \cdot 10^{-2}$	0.3808238

145

Table 3: Parameters of the single component adsorption isotherms for the ternary system Methane(1)/Nitrogen(2)/Carbon Dioxide(3) on activated carbon Norit R1 at 298 K (Dreisbach et al., 1999) and ternary system Methane(1)/Ethane(2)/Ethylene(3) on activated carbon BPL at 301.4 K (O'Brien and Myers 1985)

	Pressure Range [kPa]	q_s	Unilan		O'Brien-Myers		
			b	s	q_s	b	σ
Adsorbent: AC Norit R1							
Methane	0-5753	9.280873	$7.544924 \cdot 10^{-4}$	2.000000	--	--	--
Nitrogen	0-5958	6.975740	$3.356512 \cdot 10^{-4}$	1.707017	--	--	--
Carbon Dioxide	0-6000	13.171592	$1.560106 \cdot 10^{-3}$	1.621091	--	--	--
Adsorbent: AC BPL							
Methane	131.7-339.2	--	--	--	5.721	$9.0023 \cdot 10^{-4}$	0.8231
Ethane	131.7-339.2	--	--	--	5.639	$1.0186 \cdot 10^{-2}$	1.1927
Ethylene	131.7-339.2	--	--	--	5.900	$6.4428 \cdot 10^{-3}$	1.1737

146

147

3.1 Binary systems

148

The adsorption of the binary system Methane(1)/Ethane(2) in BPL activated carbon is analysed, regressing the data with Dual Langmuir (DL) and Toth isotherms adopting parameters of Table 2. Table 4 shows a comparison of the experimental data with the equilibria predicted by IAST using same isotherms (DL-DL or Toth-Toth) for both the components.

151

152

Table 4: Methane(1)/Ethane(2) adsorption in BPL Activated Carbon at 301.4 K (He et al., 2004). Experimental data and results from the calculation of IAST equations using DL and Toth isotherms

Pressure [kPa]	y_1	exp. data	Calculation Times [s]							
			$q_1 (x_1)$		$q_2 (x_2)$		DL		Toth	
			DL	Toth	DL	Toth	min IAST	trad. IAST	min IAST	trad. IAST
52.02	0.716	0.158 (0.119)	0.166 (0.127)	0.165 (0.124)	-5.3 (-6.6)	-4.0 (-4.5)	0.032	0.438	0.047	0.566
197.05	0.716	0.347 (0.139)	0.361 (0.149)	0.358 (0.144)	-4.1 (-6.9)	-3.0 (-3.5)	0.031	0.566	0.031	0.703
682.61	0.716	0.673 (0.174)	0.649 (0.166)	0.624 (0.162)	3.6 (4.6)	7.8 (6.9)	0.031	0.660	0.062	0.701
1397.62	0.716	0.853 (0.187)	0.801 (0.172)	0.799 (0.172)	6.1 (8.2)	6.7 (8.4)	0.031	0.548	0.047	0.665
52.3	0.906	0.262 (0.317)	0.294 (0.338)	0.278 (0.328)	-12.4 (-6.8)	-5.7 (-3.7)	0.032	0.336	0.031	0.451
683.68	0.906	1.319 (0.423)	1.289 (0.415)	1.258 (0.405)	2.3 (3.3)	4.9 (5.7)	0.032	0.609	0.047	0.699
52.18	0.97	0.331 (0.531)	0.382 (0.623)	0.357 (0.604)	-15.4 (-17.3)	-7.2 (-13.8)	0.047	0.293	0.046	0.371
195.85	0.97	0.850 (0.608)	0.909 (0.650)	0.905 (0.644)	-7.0 (-7.0)	-6.1 (-6.0)	0.032	0.375	0.031	0.478
684.88	0.97	1.820 (0.692)	1.826 (0.691)	1.814 (0.683)	-0.3 (0.0)	0.3 (1.3)	0.047	0.461	0.047	0.574
1396.82	0.97	2.539 (0.717)	2.511 (0.711)	2.467 (0.702)	1.1 (0.9)	2.9 (2.1)	0.032	0.540	0.062	0.575

Notes:

$$q\% = 100(q_{\text{exp}} - q_{\text{calc}}) / q_{\text{exp}}; x\% = 100(x_{\text{exp}} - x_{\text{calc}}) / x_{\text{exp}}$$

min IAST= minimized IAST equations

trad. IAST= IAST equations solved with the traditional approach (Do, 1998; Myers and Valenzuela 1986; Valenzuela and Myers, 1989)

153

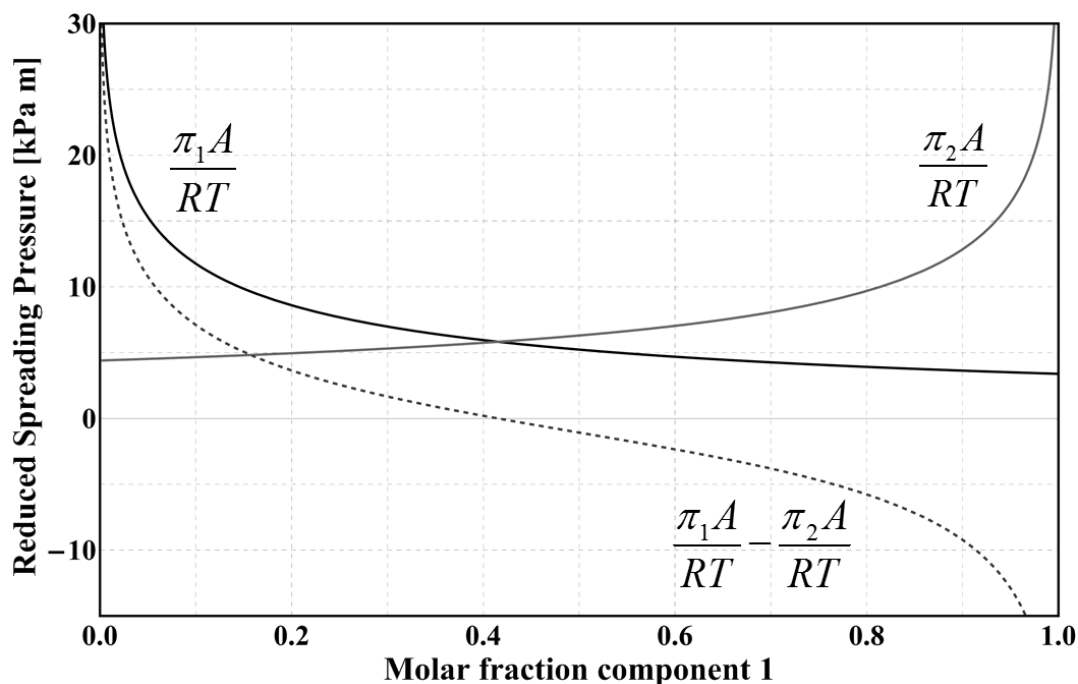
154

These results are presented in order to evaluate the advantage of the proposed solution method compared with the experimental approach of Myers (Myers and Valenzuela, 1986; Valenzuela and Myers, 1989) and

155

156 Do (Do, 1998) for the IAST equations solution. The main advantages of such new procedure are simplicity
 157 and calculation times lower than the traditional approach of about one order of magnitude which make the
 158 minimisation approach applied to binary systems adsorption comparable with the FASTIAS presented by
 159 O'Brien and Myers in (O'Brien and Myers, 1988).

160 Approaching the solution of eq.(8) as a minimisation problem has the following advantages: (i) it mitigates
 161 the necessity of an initial guess to apply the Newton method, substituting it with a set of initial points. This
 162 means that the solution is not affected by the closure of the initial condition to the final solution; (ii) the
 163 inversion of the spreading pressure function; (iii) the solution of an algebraic nonlinear system of equations.
 164 The problem is visualized in Figure 1 where the spreading pressure curves are plotted as a function of the
 165 molar fraction of methane.
 166



167
 168 Figure 1: Reduced spreading pressure curves and reduced spreading pressure difference curve obtained using
 169 DL isotherms. The curves are calculated from the data of (He et al., 2004) for the binary system
 170 methane(1)/ethane(2) on BPL activated carbon at 301.4K, 683.68kPa and molar fraction $y_1=0.906$.
 171

172 The equilibrium is represented by the value of the molar fraction where the spreading pressure difference
 173 curve has zero value. Because of high nonlinearity of the spreading pressure curves, it is more convenient to
 174 adopt a minimisation algorithm instead of trying to solve numerically the equation. Moreover, adopting eq.
 175 (8) instead of the difference curve the objective function assumes only one minimum. So even local
 176 optimization algorithms are suitable to find the correct solution.
 177

178 3.2 Ternary systems

179 Unilan and O'Brien and Myers (OM) isotherms are used for the calculation of adsorption equilibrium in
 180 ternary systems. The system Methane(1)/Ethane(2)/Ethylene(3) on activated carbon BPL (O'Brien and
 181 Myers, 1985) was studied with the OM isotherm and the system Methane(1)/Nitrogen(2)/Carbon Dioxide(3)
 182 on activated carbon Norit R1 (Dreisbach et al., 1999) with the Unilan isotherm. This first system enables a
 183 direct comparison between the FASTIAS solution method reported in (O'Brien and Myers, 1988) and the
 184 approach proposed here, in terms of calculation times. Table 5 collects the results of the calculations.
 185
 186
 187
 188
 189
 190
 191
 192

Table 5: Methane(1)/Ethane(2)/Ethylene(3) adsorption on BPL Activated Carbon at 301.4 K (O'Brien and Myers, 1985) and Methane(1)/Nitrogen(2)/Carbon Dioxide(3) on activated carbon Norit R1 at 298 K (Dreisbach et al., 1999). Experimental data and results from the calculation of IAST equations using Unilan and O'Brien and Myers isotherms.

Pressure [kPa]	y_1	y_2	experimental data		calculated values		Errors		Calculation times [s]		
			$q_1(x_1)$	$q_2(x_2)$	$q_1(x_1)$	$q_2(x_2)$	$q_1\%$ ($x_1\%$)	$q_2\%$ ($x_2\%$)	min IAS	trad IAS	FASTIAS
Methane(1)/Nitrogen(2)/Carbon Dioxide(3)											
			Unilan								
113	0.445	0.504	0.511 (0.553)	0.199 (0.215)	0.566 (0.612)	0.191 (0.181)	-10.8 (-10.7)	15.8 (15.8)	0.203	0.150	--
433	0.535	0.125	1.469 (0.415)	0.060 (0.017)	1.200 (0.333)	0.071 (0.020)	18.3 (19.7)	-18.4 (-16.3)	0.249	0.343	--
467	0.349	0.403	0.942 (0.298)	0.228 (0.072)	0.930 (0.291)	0.274 (0.086)	1.2 (2.3)	-20.3 (-18.9)	0.218	0.396	--
1054	0.538	0.115	1.994 (0.361)	0.077 (0.014)	1.760 (0.310)	0.091 (0.016)	11.8 (14.2)	-17.5 (-14.2)	0.234	0.604	--
Methane(1)/Ethane(2)/Ethylene(3)											
			O'Brien and Myers								
339.2	0.624	0.174	0.493 (0.156)	0.231 (0.469)	0.411 (0.134)	1.491 (0.484)	16.6 (14.4)	-0.6 (3.3)	0.156	0.613	0.037
124.1	0.2	0.192	0.049 (0.019)	0.014 (0.278)	0.064 (0.024)	0.821 (0.312)	-29.4 (27.0)	-14.3 (12.2)	0.156	0.422	0.043
131.7	0.23	0.52	0.059 (0.021)	0.044 (0.747)	0.068 (0.025)	2.055 (0.736)	-16.4 (16.8)	1.7 (1.4)	0.156	1.619	0.042

Notes:
 $q\% = 100(q_{exp} - q_{calc})/q_{exp}$
 $x\% = 100(x_{exp} - x_{calc})/x_{exp}$

193

194

195

196

197

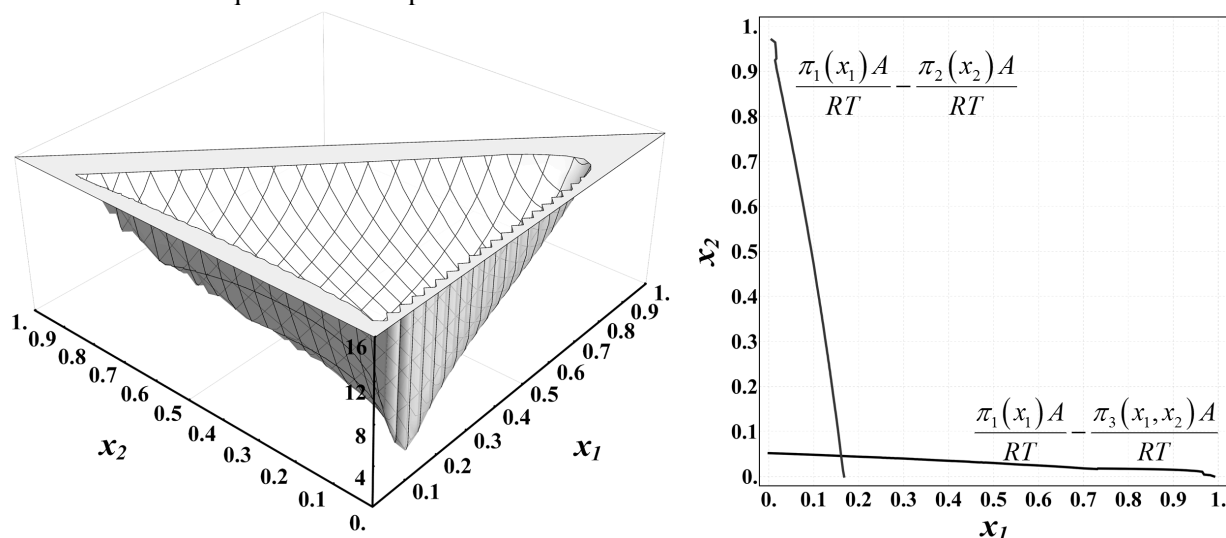
198

199

200

201

Similarly to the binary equilibrium, the ternary equilibrium can be described by the objective function of eq. (7). This objective function is a surface which, after the substitution of eq. (2), is a function of two independent molar fractions (x_1 , x_2). Figure 2 shows an illustrative example of objective function surface. It is convex and it has only a minimum whose coordinates are the equilibrium compositions. Because of the absence of additional local minima, also in this case the objective function can be easily explored by whatever local or global minimisation algorithm. A different representation of the problem is reported also in Fig. 3, where the reduced spreading pressure difference curves are shown. The intersection point of the two curves identifies the equilibrium compositions.



202

203

204

205

206

207

Figure 2: Objective function of eq. (7) (left) and reduced spreading pressure difference curves ($\pi_1 - \pi_2$) and ($\pi_2 - \pi_3$) (right) calculated using the Unilan isotherm for the ternary system Methane(1)/Nitrogen(2)/Carbon Dioxide(3) on activated carbon Norit R1 (Dreisbach et al. 1999) at 467kPa, 298K and compositions of the gaseous mixture (0.349; 0.403; 0.248).

208

209

210

211

212

The advantage of the presented procedure over the traditional one consists also in shorter computational times even if the FASTIAS method of solution remains the fastest solution. The computational speed assumes a fundamental importance when the IAST equations are applied to the dynamic modelling of adsorbent beds where the equilibrium calculations must be repeated for several time steps (Rubiera Landa et al. 2013; Santos et al. 2011).

213

214

215

216

217

As reported in Table 4 and Table 5, the calculation times are lower than the times required by the traditional solution approach, comparable to FASTIAS approach for binary mixtures adsorption and higher up to 4.2 times than the FASTIAS approach for ternary mixtures adsorption. However these times could be further reduced selecting more effective minimisation algorithms tailored on this specific problem.

218

4. Conclusions

219

220

221

222

An alternative procedure for the solution of the IAST equations was proposed. The procedure is based on the minimisation of the iso-spreading pressure condition and leads to values close to the experimental equilibrium concentrations without any involvement of spreading pressure inversion and initial guess, which are the typical requirements of the presently adopted solution approaches.

223 The procedure was tested on binary and ternary systems adsorption using Dual Langmuir, Toth, Unilan and
224 O'Brien and Myers isotherms. A comparison with the most used existing solution procedures was presented
225 in terms of calculation times which are fundamental in theoretical studies of adsorbent bed dynamics.
226 In terms of calculation times, the proposed solution procedure is quicker than the traditional solution method
227 (Do, 1998; Myers and Valenzuela 1986; Valenzuela and Myers, 1989). Calculation times become
228 comparable to the FASTIAS method (O'Brien and Myers, 1988) for binary systems adsorption.
229

230 5 Acknowledgements

231 This work has received funding from the European Union's Seventh Programme for research, technological
232 development and demonstration, under Marie Curie Career Integration Grant Agreement No PCIG14-GA-
233 2013-630863 (Atmospheric Carbon CApture).
234

235 6. Nomenclature

236	P	Pressure [kPa]
237	P_{tot}	Total pressure of the non-adsorbed mixture [kPa]
238	P_i^0	Surface pressure of the component i [kPa]
239	y_i	Molar fraction of the component i in the non-adsorbed mixture
240	x_i	Molar fraction of the component i in the adsorbed mixture
241	q_i^0	Specific amount adsorbed of component i in the adsorbent at equilibrium [mol/kg]
242	π_i^0	Spreading pressure of the component i at equilibrium [kPa m]
243	A	Specific surface area covered by the adsorbed mixture [m ² /kg]
244	R	Universal gas constant [kJ/(mol K)]
245	T	Equilibrium temperature [K]
246	NC	Number of components participating in the adsorption
247	q_i	Specific amount adsorbed of component i in the adsorbent [mol/kg]
248	q_{tot}	Specific amount adsorbed of mixture [mol/kg]
249	f_{binary}	Objective function in the case of binary mixture
250	f_{ternary}	Objective function in the case of ternary mixture

251

252 7. References

253

254 Cessford NF, Seaton NA, Düren T. Evaluation of Ideal Adsorbed Solution Theory as a Tool for the Design
255 of Metal-Organic Framework Materials. *Ind Eng Chem Res* 2012;51:4911-4921.

256

257 Dawoud B, Hoefle P, Bornmann A, Chmielewski S, Marburger C. Vacuum sorption apparatus. patent
258 publication number: WO2012041265, 2012-04-05.

259

260 Do DD. *Adsorption Analysis: Equilibria and Kinetics*. London: Imperial College Press; 1998.

261

262 Dreisbach F, Staudt R, Keller JU. High Pressure Adsorption Data of Methane, Nitrogen, Carbon Dioxide and
263 their Binary and Ternary Mixtures on Activated Carbon. *Adsorption* 1999;5:215-227.

264

265 Frey DD, Rodrigues AE. Explicit calculation of multicomponent equilibria for ideal adsorbed solutions.
266 *AIChE J* 1994;40:182-186.

267

268 Gritti F, Guiochon G. Band splitting in overloaded isocratic elution chromatography: II. New competitive
269 adsorption isotherms. *J Chromatogr A* 2003;1008:23-41.

270

271 Gritti F, Guiochon G. New thermodynamically consistent competitive adsorption isotherm in RPLC. *J*
272 *Colloid Interface Sci* 2003;264:43-59.

273

274 He Y, Yun JH, Seaton NA. Adsorption equilibrium of binary methane/ethane mixtures in BPL activated
275 carbon: isotherms and calorimetric heats of adsorption. *Langmuir* 2004;20:6668-6678.

276

277 Ilic M, Flockerzi D, Seidel-Morgenstern A. A thermodynamically consistent explicit competitive adsorption
278 isotherm model based on second-order single component behaviour. *J Chromatogr A* 2010;1217:2132-2137.

279
280 LeVan MD, Vermeulen T. Binary Langmuir-like and Freundlich isotherms for ideal adsorbed solutions. *J.*
281 *Phys Chem* 1981;85:3247-3250.
282
283 Liu Z, Grande CA, Li P, Yu J, Rodrigues AE. Multi-bed Vacuum Pressure Swing Adsorption for carbon
284 dioxide capture from flue gas. *Sep Purif Technol* 2011;81:307-317.
285
286 Minceva M, Rodrigues AE. Two-level Optimization of an Existing SMB for p-Xylene Separation. *Comput*
287 *Chem Eng* 2005;29:2215-
288
289 Mota JPB, Rodrigo AJS. Calculations of Multicomponent Adsorption-Column Dynamics Combining the
290 Potential and Ideal Adsorbed Solution Theories. *Ind Eng Chem Res* 2000;39:2459-2467
291
292 Myers AL, Prausnitz JM. Thermodynamics of mixed-gas adsorption. *AIChE J* 1965;11:121-127.
293
294 Myers AL, Valenzuela D. Computer Algorithm for Calculating Adsorption Equilibria of Gas Mixtures. *J*
295 *Chem Eng Jpn* 1986;19:392-396.
296
297 Nelder JA, Mead R. A Simplex Method for Function Minimization. *Comput J* 1965;7:308-313.
298
299 O'Brien JA, Myers AL. Rapid Calculations of Multicomponent Adsorption Equilibria from Pure Isotherm
300 Data. *Ind Eng Chem Process Des Dev* 1985;24:1188-1191.
301
302 O'Brien JA, Myers AL. A comprehensive technique for equilibrium calculations in adsorbed mixtures: the
303 generalized FastIAS method. *Ind Eng Chem Res* 1988;27:2085-2092.
304
305 Ramaswamy S, Huang HJ, Ramarao BV. *Separation and Purification Technologies in Biorefineries*. 1st ed.
306 The Atrium, Southern Gate, Chichester: John Wiley & Sons; 2013.
307
308 Rubiera Landa HO, Flockerzi D, Seidel-Morgenstern A. A method for efficiently solving the IAST equations
309 with an application to adsorber dynamics. *AIChE J* 2013;59:1263-1277.
310
311 Santori G, Frazzica A, Freni A, Galieni M, Bonaccorsi L, Polonara F, Restuccia G. Optimization and testing
312 on an adsorption dishwasher. *Energy* 2013;50:170-176.
313
314 Santori G, Santamaria S, Sapienza A, Brandani S, Freni A. A stand-alone solar adsorption refrigerator for
315 humanitarian aid. *Solar Energy* 2014;100:172-178.
316
317 Santos JC, Cheng Y, Dias MM, Rodrigues AE. Surface B-Splines fitting for Speeding Up the Simulation of
318 Adsorption Processes with IAS Model. *Comput Chem Eng* 2011;35:1186-1191.
319
320 Tarafder A, Mazzotti M. A Method for Deriving Explicit Binary Isotherms Obeying the Ideal Adsorbed
321 Solution Theory. *Chem Eng Technol* 35 (2012) 102-108.
322
323 Valenzuela DP, Myers AL. *Adsorption Equilibrium Data Handbook*. 4th ed. Englewood Cliffs: Prentice
324 Hall; 1989.
325
326 Yun JH, Düren T, Keil FJ, Seaton NA. Adsorption of methane, ethane, and their binary mixtures on MCM-
327 41: an experimental evaluation of methods for the prediction of adsorption equilibrium. *Langmuir*
328 2002;18:2693-2701.
329
330 Yu N, Wang RZ, Wang LW. Sorption thermal storage for solar energy. *Prog Energy Comb Sci* 2013;39:489-
331 514.