Adsorption (2014) 20:555–563
DOI 10.1007/s10450-013-9600-x

Modeling adsorption in binary associating solvents using the extended MPTA model

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Received: 20 June 2013 / Revised: 5 November 2013 / Accepted: 30 December 2013 / Published online: 7 January 2014

Abstract Application of the MPTA model has been extended to associative liquid adsorption. The MPTA model describes fluid–fluid interactions using an equation of state (EoS) term, and fluid–solid interactions using a potential equation. In order to extend the application to associative liquid adsorption, an association term has been considered for fluid–fluid interactions. Sixteen binary mixtures containing associating and non-associating components in equilibrium with various adsorbents have been studied; fluid–fluid interactions have been modeled using the Peng–Robinson, Soave–Redlich–Kwong, volume-translated SRK and CPA equations of state, while the effects of fluid–solid interactions have been taken into account using Dubinin–Radushkevich–Astakhov (DRA) and Steele potential functions. The model parameters have been obtained by fitting the model to experimental data on surface excess. For the studied systems, the accuracy of fitted isotherms has been found to be more dependent on the fluid–solid potential equation rather than the applied EoS. Calculations show that the SRK equation is a suitable choice for non-associating systems, while the CPA equation is found to be more appropriate for associating systems, as would be expected. The results also show that the Steele potential function is in better agreement with experimental data than the DRA potential function.

Keywords MPTA model · Adsorption · CPA · Aromatics · Equation of state

List of symbols

AARD	Average absolute relative deviation, $\frac{100}{N}\sum\left\lvert\frac{n_i^{e,\exp}-n_i^{e,calc}}{n_i^{e,\exp}}\right\rvert$
N	Number of experimental data
P	Pressure (bar)
$P(z)$	Pressure at given z value (bar)
x_B	Mole fraction of bulk phase
$x(z)$	Mole fraction of adsorbed phase at given z value
z	Distance (cm) or pore volume ($\mathrm{cm^3/g_{ads}}$)

Greek letters

ε_i	Adsorption potential of "*i*" specie (J/mol)
φ_i	Fugacity coefficient of "*i*" specie
μ_i	Chemical potential of "*i*" specie (J/mol)
$\rho(z)$	Density of adsorbed phase at given z value
ρ_B	Density of bulk phase
$\Gamma_i^{(n)}$	Surface excess of "i" specie ($\mathrm{mol/g_{ads}}$)

Abbreviations

AARD	Absolute average relative deviation
ASST	Adsorbate solid solution theory
CPA	Cubic plus association
DRA	Dubinin–Radushkevich–Astakhov
EoS	Equation of state
IAST	Ideal adsorbed solution theory
MPTA	Multicomponent potential theory of adsorption
PAH	Polycyclic aromatic hydrocarbon
PR	Peng–Robinson
PTA	Potential theory of adsorption
RAST	Real adsorbed solution theory
SRK	Soave–Redlich–Kwong

Electronic supplementary material The online version of this article (doi:10.1007/s10450-013-9600-x) contains supplementary material, which is available to authorized users.

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VOC	Volatile organic compound
VST	Vacancy solution theory
VT-SRK	Volume translated Soave–Redlich–Kwong

1 Introduction

Chemical and petrochemical wastewaters contain effluents such as aromatics, PAH's and VOC's. These components impose adverse effects on the ecology, as well as direct effects on human beings; one well-known syndrome is the Good Pasture syndrome which is caused by aromatics (Lin and Huang 1999; Khanal 2003). Aromatics can also be found in petrol and diesel fuel, and the leakage of these contaminants from underground storage tanks can be very harmful to underground water quality (Daifullah and Girgis 2003). Therefore, rigid rules are set up in order to reduce these components from industrial effluents, and the industries are constantly on the search for technically and economically feasible ways to eliminate them. Recent advances in this area include the application of bio-filtration, bioremediation, membrane processes, and adsorption (Sene et al. 2002; Soares et al. 2010; Frahn et al. 2004).

Recently, many investigations have been reported on different aspects of adsorption (c.f. [7–21]). Adsorption processes can be utilized as feasible methods for removing the impurities. A wide range of adsorbents are applicable in this regard, and based on availability and demand, effective adsorbents can be made either from natural sources, such as rice husk or fruit (e.g. durian) shells, or from various polymeric material (Nevin Yalcin 2000; Tham et al. 2011; Long et al. 2010). However, carbonaceous adsorbents are one of most effective adsorbents because of the diverse availability of raw materials, high specific surface area, and also because of the fact that they can be readily modified for selective adsorption (Yin et al. 2007).

On the other hand, in order to improve and optimize the aforementioned phenomena, accurate modeling of the adsorption process has been one of the main challenges for researchers in this field (Suzuki 1990). The ideal adsorbed solution theory (IAST), proposed by Myers and Prausnitz, is one of the best known theories for prediction of adsorption, which considers the adsorbed phase as an ideal solution (Myers and Prausnitz 1965). In order to take into account the non-ideality of the adsorbing phase, theories like real adsorbed solution theory (RAST) and vacancy solution theory (VST) have been developed and used for different systems (Ruthven 1976; Fukuchi 1982), giving improved results for non-ideal mixtures. Berti et al. have also proposed a model involving activity coefficients, and the model considers the adsorbent as a component in mixture: this so-called adsorbate–solid-solution-theory (ASST) concept leads to a thermodynamically consistent description regarding adsorption equilibrium and caloric properties (Berti et al. 2000). Among various other modeling attempts, Kalies et al. proposed a modification of Porter's equation (Kalies et al. 2000), Lee et al. proposed a model based on two dimensional adsorbed phase equation of state (Lee and Belfort 1988), and Khan et al. suggested a model based on principles of solution thermodynamics for liquid–solid equilibrium, and used the Redlich–Kister expansion for predicting the activity coefficient of solids (Khan et al. 2000).

The multi-component potential theory of adsorption (MPTA) is also considered as an alternative approach, the main idea of this model was proposed by Dubinin et al., called the potential theory of adsorption (PTA; Dubinin and Astakhov 1971). The model was extended to multi-component adsorption by Shapiro and Stenby (1998), and Monsalvo and Shapiro (2007a) who have also shown that the theory is appropriate for modeling of adsorption in micro porous media (Monsalvo and Shapiro 2007a). While the model considers the adsorbates as a segregated mixture in the external field of potential (caused by the adsorbent), the bulk phase is not considered to be influenced by the adsorbent. This approach makes it possible to model the thermodynamics of the two phases using an equation of state (EoS) and a solid–fluid potential function for modeling fluid–fluid and solid–fluid interactions, respectively. As an advantage, the model can be applied to either gas or liquid mixtures.

In this work, various EoS's and potential functions have been applied in the framework of the MPTA model, in order to study the effect of each term. Special attention has been given to associating molecules such as water and alcohols, where applying a Cubic-Plus-Association (CPA) EoS (Kontogeorgis et al. 1999) can improve the prediction of fluid–fluid behavior. Application of the MPTA model has also been extended to non-carbonaceous adsorbents. In the first section of the work, principles of MPTA method are briefly described. In the second section, results of applying the MPTA model to associating and non-associating have been studied.

2 Theory and calculations

2.1 Description of the model

The MPTA model has been developed initially by considering the adsorption process happening on a plane surface, from a bulk phase with pressure P_B and mole fraction of x_B. At distance z from the adsorbent, the potential field between adsorbent and each component is affected by its own potential, $\varepsilon_i(z)$ (Monsalvo and Shapiro 2007b). This potential not only depends on the distance from the surface of adsorbent, but also on the component type, and it varies from one component to another (Monsalvo and Shapiro 2009a). The equilibrium condition happens when, at a certain temperature, the following equation is satisfied:

$$\mu_i(P(z), x(z)) - \varepsilon_i(z) = \mu_{iB}(P_B, x_B) \quad i = 1, \ldots, n \tag{1}$$

where μ_i is the chemical potential of the adsorbed phase, μ_{iB} is the chemical potential of the bulk phase, and $\varepsilon_i(z)$ is the adsorption potential. In this approach, the adsorbed phase is assumed to be an inhomogeneous mixture, and fluid–fluid interactions and solid–fluid interactions are modeled by the first and second terms of the left hand side of the equation, respectively. We can simplify Eq. (1) by using fugacity coefficients instead of chemical potentials, resulting in the following equation:

$$x_i(z) = \frac{x_{Bi}\varphi_{Bi}P_B \exp(\varepsilon_i(z)/RT)}{\varphi_i(\rho(z), x(z))P(z)} \quad i = 1, \ldots, n \tag{2}$$

Extending equation (2) to all phases and summing up terms results in:

$$P(z) = \sum_{i=1}^{n} \frac{x_{Bi}\varphi_{Bi}P_B \exp(\varepsilon_i(z)/RT)}{\varphi_i(\rho(z), x(z))} \quad i = 1, \ldots, n \tag{3}$$

At a given pressure and mole fraction of bulk phase (P_B, x_B), the pressure and mole fraction of adsorbed phase can therefore be determined. The main idea behind the MPTA model is that the chemical potential of the adsorbed phase is given by the sum of fluid–fluid and fluid–solid interactions. Thereupon, we can incorporate different EoS's with different fluid–solid potential functions.

In case of micro-pore adsorption, parameter z represents the porous volume rather than distance from the surface of adsorbent. The distribution of the porous volume can be represented by $z(\varepsilon_i)(\mathrm{cm}^3/\mathrm{g_{ads}})$ (instead of $\varepsilon_i(z)$) which can be calculated by the Dubinin–Radushkevich–Astakhov (DRA) equation (Stoeckli 1998). DRA is a semi-empirical equation which was initially used for adsorption of gases and vapors on porous carbonaceous adsorbents, and later on extended to various other components:

$$z(\varepsilon_i) = z_0 \exp\left(-\frac{\varepsilon_i}{\varepsilon_{0i}}\right)^{\beta} \tag{4}$$

z_0 and ε_{0i} stand for adsorption capacity and characteristic energy, respectively. The adsorption capacity is related to the porous volume; the concept of porous volume is very important, yet not well understood, and in the context of the theory it is treated as an effective parameter. The characteristic energy parameter is an energy parameter depending on average pore width, and it characterizes the solid–fluid interaction strength. The adsorption energy ε_i is a function of the variable $RTln(P_0/P_B)$, where P_0 is the vapor pressure of pure component at temperature T. Parameter β represents the heterogeneity of pores; generally the value of this parameter is two for carbonaceous adsorbents, three for molecular sieves, silicates and silica gels and may vary up to 7 for other components (Monsalvo and Shapiro 2007a, 2009a). It is suggested that the DRA equation is suitable for narrow pore size distributed adsorbents, and for wider ranges of pore size distribution it may not be very applicable (Fukuchi 1982). In previous works, it is assumed that the value of z_0 is constant and equal for all of the species in the mixture. Therefore, Eq. (4) can be written as:

$$\varepsilon_i(z) = \varepsilon_{0i} \ln\left(\frac{z_0}{z}\right)^{1/\beta} \tag{5}$$

Recently Monsalvo and Shapiro (2009a) have applied the Steele potential function instead of DRA. Unlike DRA, this equation has two terms for repulsion and attraction. The porous media is considered to be a collection of independent slit-like pores. Each pore is consisted of two infinite parallel walls in the x–y direction. The distance of these walls in the z direction is H. Both walls are taken to be a basal planes of graphite-like surface (for carbonaceous adsorbents) and silicon-dioxide surface (for silicium-used adsorbents), made up of Lennard-Jones atoms of diameter σ_s hexagonally arranged at each plane for carbonaceous adsorbents, and trigonally for silicium-based adsorbents. In the case of a planar graphite surface, the graphite layers are separated by a uniform distance $\Delta = 0.335$ nm. This value is 161 nm for silicium-based adsorbents (Wells and Wells 1975). The wall potential is calculated by integration, assuming Lennard-Jones potential for fluid–solid atoms. The result is given as follows:

$$u_{sf,i}(z) = 2\pi\rho_s\varepsilon_{sf,i}\sigma_{sf,i}^2\Delta\left[\frac{2}{5}\left(\frac{\sigma_{sf,i}}{z}\right)^{10} - \left(\frac{\sigma_{sf,i}}{z}\right)^{4} - \left(\frac{\sigma_{sf,i}^4}{3\Delta(z+0.61\Delta)^3}\right)\right] \tag{6}$$

The terms with powers of 10 and four represent the repulsive and attractive solid–fluid interactions. The last term on the right hand side of Eq. (6) represents the total remained attractive interactions between solid and fluids on remaining layers of adsorbent. The mixture solid–fluid interaction parameter $\sigma_{sf,i}$ is obtained using Lorentz–Berthelot mixing rule:

$$\sigma_{sf,i} = (\sigma_s + \sigma_{f,i})/2 \tag{7}$$

where the subscripts s and f represent the solid and fluid, respectively. In all calculations of carbonaceous adsorbents and silicium-based adsorbents, graphite parameters and silicon dioxide parameters were used, respectively, following Balilehvand et al. (2012) and Wells and Wells

(1975). The number of molecules per unit volume of silicon dioxide molecules, assuming spherical shape, is calculated as $\rho_s = 57.2\ \mathrm{nm}^{-3}$. The fluid parameters are reported in refs. (Poiling et al. 2000; Chae and Violi 2011). The fluid–solid interaction parameters can be obtained by applying the Lorentz–Berthelot mixing rule (where diameters of fluid atoms are assumed to be Lennard-Jones diameters):

$$\varepsilon_{sf,i} = \left(\varepsilon_s \varepsilon_{f,i}\right)^{1/2} \tag{8}$$

$$\varepsilon_s / k_B = 28.0\,K \tag{9}$$

It should be noted that in this approach, $\varepsilon_{sf,i}$ is considered to be an effective parameter which is adjusted using adsorption data. For a given slit pore of width H_0, a molecule of fluid interacts with both of walls. Thereupon, the potential value is given as:

$$\varepsilon_i(z) = u_{sf,i}(z) + u_{sf,i}(H_0 - z) \tag{10}$$

This equation gives the value of solid–fluid potential. In order to obtain the interaction energy of one mole fluid and solid, it should be multiplied by the Avogadro number.

2.2 Surface excess and adsorption isotherms

In most of adsorption experiments at equilibrium condition, it is common to use surface excess instead of absolute amounts. According to definition of surface excess (Monsalvo and Shapiro 2007b), the surface excess is the difference between total amount of adsorbed component and the amount of that component which would be present in the adsorbed phase if the properties of adsorbed phase were the same as those of equilibrium bulk phase. In liquid adsorption, generally, the surface excess is considered to be:

$$\Gamma_i^{(n)} = n_{B0}(x_{B0i} - x_{Bi}) \tag{11}$$

where n_{B0} (mol/g$_{\mathrm{ads}}$) is total amount of moles in liquid before immersion of solid, x_{B0i} and x_{Bi} are mole fractions of component i before and after immersion of solid in liquid mixture. By applying mass balance over adsorbed phase, we can rewrite the above equation as:

$$\Gamma_i^{(n)} = n_A(x_{Ai} - x_{Bi}) \tag{12}$$

where n_A (mol/g$_{\mathrm{ads}}$) and x_{Ai} are number of moles and mole fraction of component i in the adsorbed phase, respectively.

According to Eq. (12) and using the DRA potential function, the surface excess is defined as follows:

$$\Gamma_i^{(n)} = \int_0^{z_0} [\rho(z)x_i(z) - \rho(z)x_{Bi}]dz \tag{13}$$

Integration should be performed on the whole porous space, from 0 to z_0. When $z \to z_0$, the adsorption potential

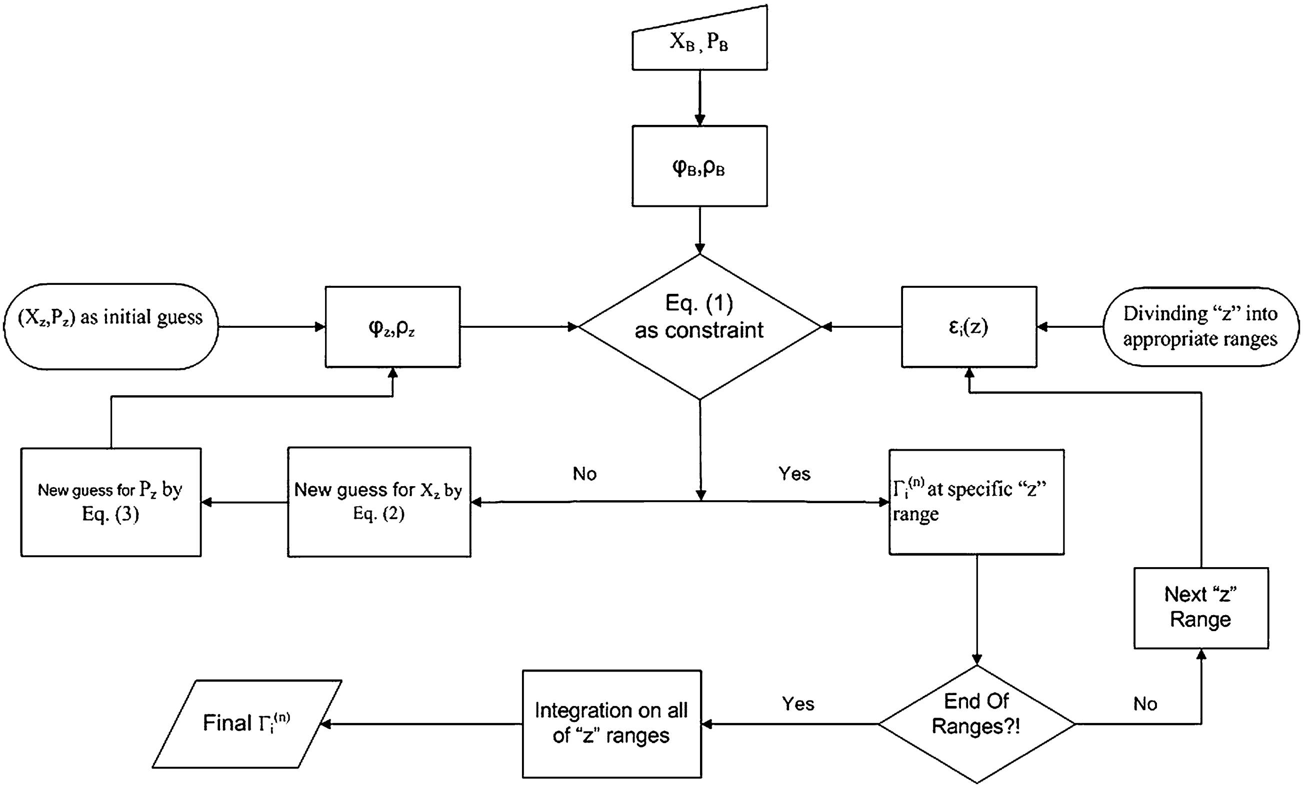

Fig. 1 MPTA diagram in case of liquid adsorption

Table 1 Absolute average relative deviations in modeling of binary systems using MPTA method, applying different EoS's and DRA potential equation

No.	System	CPA (%)	SRK (%)	VT-SRK (%)	PR (%)	Temperature (K)	References
1	Benzene/cyclohexane AC	25.62	5.49	21.62	22.83	303.15	Monsalvo and Shapiro (2009a)
2	Benzene/cyclohexane CB	43.64	6.79	6.59	6.59	303.15	Monsalvo and Shapiro (2009a)
3	Benzene/ethanol AC	15.69	4.04	10.83	12.04	303.15	Monsalvo and Shapiro (2009a)
4	Benzene/2-propanol (N-950)	10.03	15.56	13.82	18.67	293.15	Świątkowski et al. (2004)
5	Benzene/2-propanol (N-1500)	23.44	22.19	21.37	24.04	293.15	Świątkowski et al. (2004)
6	Benzene/2-propanol (N-1800)	33.18	34.22	35.89	39.13	293.15	Świątkowski et al. (2004)
7	Benzene/ethyl acetate AC	15.35	12.18	12.08	14.54	303.15	Monsalvo and Shapiro (2009a)
8	Acetone/benzene (SiO_2-200)	9.76	16.88	18.24	18.66	298	Goworek and Nieradka (1996)
9	Acetone/benzene (SiO_2-800)	10.15	15.65	17.03	17.33	298	Goworek and Nieradka (1996)
10	Acetone/*n*-heptane (SiO_2-200)	17.10	13.30	17.93	15.78	298	Goworek and Nieradka (1996)
11	Acetone/*n*-heptane (SiO_2-800)	17.09	13.33	17.19	17.63	298	Goworek and Nieradka (1996)
12	Benzene/cyclohexane SG	11.80	5.62	8.05	9.32	273.15	Monsalvo and Shapiro (2009a)
13	Benzene/cyclohexane SG	9.49	3.55	4.89	5.32	303.15	Monsalvo and Shapiro (2009a)
14	Benzene/cyclohexane SG	8.45	2.74	3.07	3.68	333.15	Monsalvo and Shapiro (2009a)
15	*n*-Octane/ethanol (SBA-15)	11.14	14.53	8.46	16.72	298	Kalies et al. (2010)
16	n-Octane/ethanol (SBA-16)	14.50	16.16	15.88	22.49	298	Rockmann and Kalies (2007)
	Total AAD	17.27	12.63	14.55	16.54		

tends to zero and properties of adsorbate in the adsorbed phase tend to the properties of this component in the bulk phase: $(z) \rightarrow \rho_B$, $(z) \rightarrow x_B$.

In the case of using the Steele potential function, the parameter z has the meaning of distance from the pore wall. Thereupon, Eq. (13) should be modified. Assuming that the porous component is a collection of pores which are not inter-connected to each other while having the same geometry of slit-pore (of width of H_0), surface excess is defined as follows:

$$\Gamma_i^{(n)} = A_s \int_{H_{\min}}^{H_{\max}} \rho(H)(x_i(H) - x_{Bi}) f(H) dH \qquad (14)$$

\where $\rho(H)$ and $x_i(H)$ represent the density and the mole fraction of component i in a pore of width H. $f(H)$ is pore size distribution and H_{min} and H_{max} are the possible range of pore widths. To simplify this equation, we assume that all of the pores have the width of H_0, thus we can ignore the pore size distribution and finally, the surface excess is given as:

$$\Gamma_i^{(n)} \approx A_s \int_{0.7\sigma_{f,i}}^{H_0 - 0.7\sigma_{f,i}} \rho(z)(x_i(z) - x_{Bi}) dH \qquad (15)$$

Integration is performed from $0.7\sigma_{f,i}$ to $H_0 - 0.7\sigma_{f,i}$. This cutoff distance of $0.7\sigma_{f,i}$ is the closest distance that molecules of fluid can get to the walls; in this way, the dead

Table 2 Absolute average relative deviations in modeling of binary systems using MPTA method, applying different EoS's and Steele potential equation

No.	System	CPA (%)	SRK (%)	VT-SRK (%)	PR (%)	T (K)	References
1	Benzene/cyclohexane AC	7.06	10.62	20.85	21.61	303.15	Monsalvo and Shapiro (2009a)
2	Benzene/cyclohexane CB	8.28	8.90	7.37	7.81	303.15	Monsalvo and Shapiro (2009a)
3	Benzene/ethanol AC	19.48	5.64	5.92	9.62	303.15	Monsalvo and Shapiro (2009a)
4	Benzene/2-propanol N-950	4.31	9.71	7.86	23.57	293.15	Świątkowski et al. (2004)
5	Benzene/2-propanol N-1500	19.07	5.90	18.95	10.45	293.15	Świątkowski et al. (2004)
6	Benzene/2-propanol N-1800	24.40	9.62	24.40	25.83	293.15	Świątkowski et al. (2004)
7	Benzene/ethyl acetate AC	10.79	4.91	13.60	5.50	303.15	Monsalvo and Shapiro (2009a)
8	Acetone/Benzene SiO_2-200	7.13	5.54	24.34	12.74	298. 15	Goworek and Nieradka (1996)
9	Acetone/benzene SiO_2-800	8.43	10.23	16.03	13.51	298.15	Goworek and Nieradka (1996)
10	Acetone/*n*-heptane SiO2-200	5.61	6.50	18.29	11.56	298.15	Goworek and Nieradka (1996)
11	Acetone/*n*-heptane SiO_2-800	5.88	6.60	14.71	9.94	298.15	Goworek and Nieradka (1996)
12	Benzene/cyclohexane SG	5.03	7.89	10.69	3.45	273.15	Monsalvo and Shapiro (2009a)
13	Benzene/cyclohexane SG	5.87	6.53	9.54	2.38	303.15	Monsalvo and Shapiro (2009a)
14	Benzene/cyclohexane SG	3.89	7.83	4.09	5.42	333.15	Monsalvo and Shapiro (2009a)
	Total AAD	9.65	7.06	14.04	11.67		

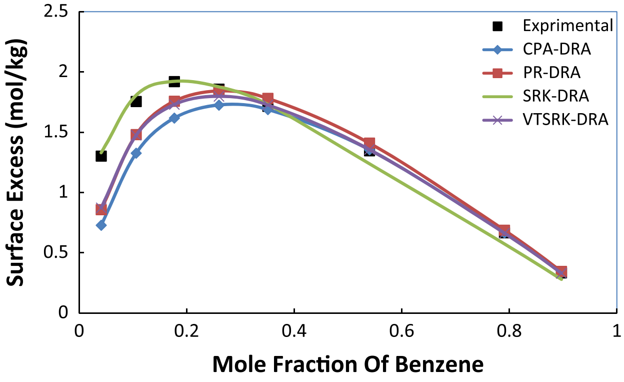

Fig. 2 Adsorption of mixture benzene/cyclohexane on SG using MPTA-DRA at T = 273.15 (Monsalvo and Shapiro 2009a)

volume near the walls is not included, but according to Monsalvo et al. the cutoff distance of $0.7\sigma_{f,i}$ is the most appropriate value (Monsalvo and Shapiro 2009b).

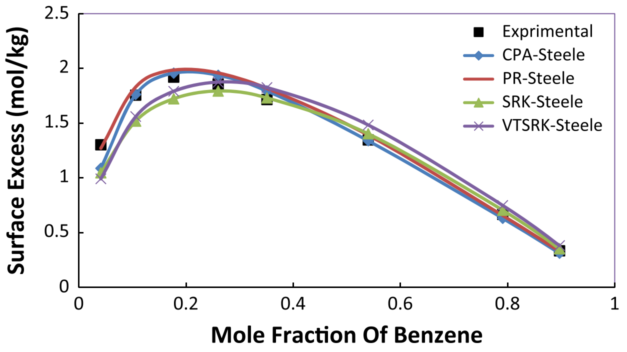

Fig. 3 Adsorption of mixture benzene/cyclohexane on SG using MPTA-Steele at T = 273.15 (Monsalvo and Shapiro 2009a)

The detailed algorithm used for calculations based on this model has been presented elsewhere (Shapiro and Stenby 1998); a simplified algorithm has been presented here in Fig. 1 for the sake of clarity.

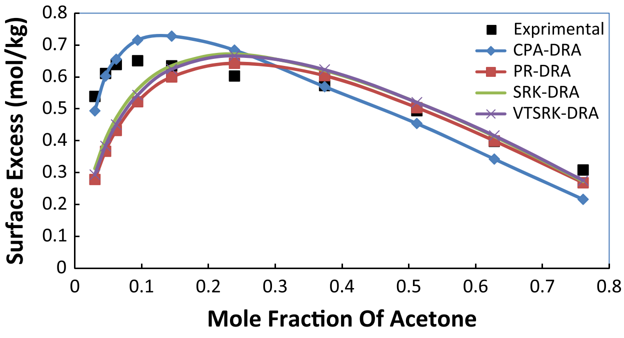

Fig. 4 Adsorption of mixture acetone/benzene on SiO_2-200 using MPTA-DRA at T = 298 (Goworek and Nieradka 1996)

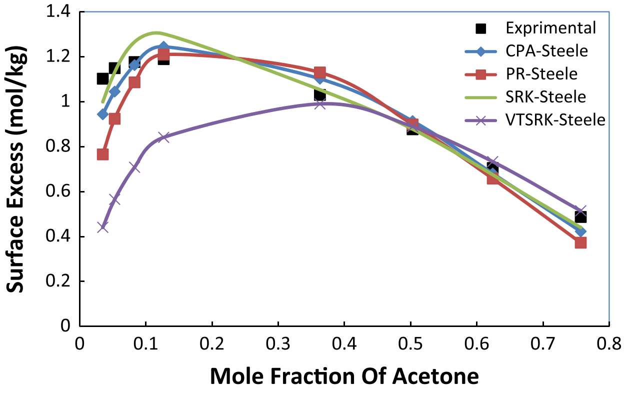

Fig. 5 Adsorption of mixture acetone/benzene on SiO_2-200 using MPTA-Steele at T = 298 (Goworek and Nieradka 1996)

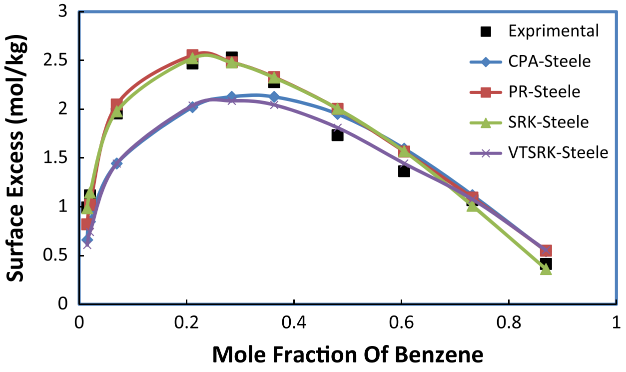

Fig. 6 Adsorption of mixture benzene/2-propanol on N-1500 using MPTA-Steele at T = 293 (Świątkowski et al. 2004)

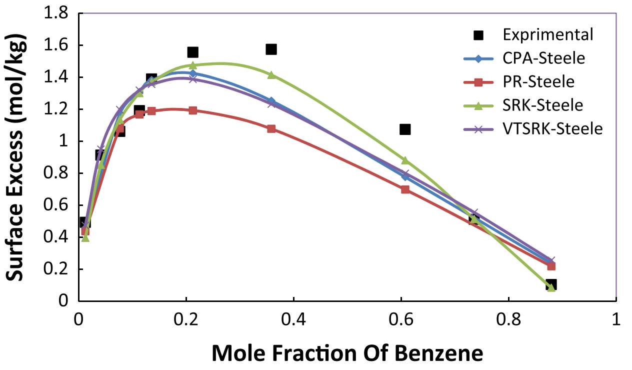

Fig. 7 Adsorption of mixture benzene/2-propanol on N-1800 using MPTA-Steele at T = 293 (Świątkowski et al. 2004)

3 Results and discussion

In this section the results of using MPTA to model the adsorption of various adsorbates on carbon and silicium-based adsorbents has been presented and compared to experimental data (Monsalvo and Shapiro 2009a; Świątkowski et al. 2004; Goworek and Nieradka 1996; Kalies et al. 2010; Rockmann and Kalies 2007). Results have been presented in Tables 1 and 2 as average absolute relative deviations (AARD) in calculated surface excess for the studied systems. Also in Tables 3 to 10 (Online Resource 1) the model parameters have been presented. In order to model fluid–fluid interactions, four EoS's including SRK (Soave 1972), PR (Peng and Robinson 1976), VT-SRK (Lin et al. 2006) and CPA (Kontogeorgis et al. 1999) were used, while fluid–solid interactions were modeled using DRA and Steele potential functions (Stoeckli 1998; Steele 1974). Classical quadratic and linear mixing rules have been applied for energy parameter (a) and co-volume parameter (b), respectively. All binary interaction parameters (k_{ij}) have been set to zero in all of calculations.

As discussed by Shapiro et al. (Monsalvo and Shapiro 2009a) for the so-called *U-shaped* isotherms in binary liquid mixtures, it is usually assumed that the interaction of adsorbed fluid with the adsorbent is greater than that of the non-adsorbed fluid. Thus, the interaction of non-adsorbed fluid with the solid phase has been ignored and the adsorption energy set to zero; $\varepsilon_2(z) = 0$. As a result, in the case of modeling with the MPTA-DRA model, there are two adjustable parameters z_0 and ε_{01}, while in the other case, three adjustable parameters (A_s, H_0 and $\varepsilon_{sf,1}$) should be estimated. In order to estimate the adjustable parameters, the objective function was minimized using a shuffled complex evolution algorithm (Duan et al. 1993).

Calculation results have also been depicted for some of the studied systems in Figs. 2, 3, 4, 5, 6. The results show that in most cases, using the Steele potential gives a better prediction compared to the DRA potential. As given in Tables 1 and 2, using the Steele potential decreases the AARD (Absolute Average Relative Deviation) in most cases. The Steele potential function models all interactions between solid and liquid as repulsive and attractive interactions, while the DRA potential function is a semi empirical equation, lacking theoretical background. The percent AARD for calculations using the MPTA model coupled with SRK EoS and DRA potential function is 12.63 %, while it decreases to 7.06 % when Steele potential function is utilized. However, for the specific case of benzene/cyclohexane at all temperatures and for all adsorbents (see Figs. 2, 3) the DRA and Steele potential functions show similar results. This can be related to the non polar behavior of benzene and cyclohexane; this phenomena has also been reported in previous studies (Bjørner et al. 2013).

In the case of cubic EoS's, our results show that the SRK EoS results in better predictions compared to PR or VT-SRK. The percent AARD of using different EoS's has been presented in Tables 1 and 2, and it can be seen that in both cases (using DRA or Steele potential function), SRK EoS shows the best performance.

Since classical cubic equations of state generally fail in the case of associating fluids, it is expected that by considering an association term, the results should be improved. Therefore the CPA EoS has been coupled with the MTPA model. Results for selected systems are depicted in Figs. 4 and 5. The results show that only in the case of polar adsorbents, considering the association term improves the performance of the model, while in the case of non-polar adsorbent, it is not a good choice. The results are in agreement with those reported previously by Bjørner et al. (2013). This may be due to the fact that in the case of polar adsorbents, the associative polar species is adsorbed into the small pores and cavities of the adsorbent. Therefore the association term in CPA EoS improves the results where self-association is significant, while in case of non-polar adsorbate on non-polar adsorbent (like the system Benzene/Ethanol depicted in Fig. 6), the non polar adsorbent does not tend to adsorb the polar species, and considering association is not effective. Besides, while hydrogen bonding in the CPA EoS is assumed to represent a continuous distribution in the fluid, it may no longer be valid in small pores and cavities, especially for non-polar adsorbent systems (Bjørner et al. 2013; Fig. 7).

4 Conclusion

In this work, binary U-shape adsorption mixtures have been studied. For some of the systems one of the components is associating. Various types of EoS coupled with two different potential functions have been utilized. For the studied systems it is found that the deviation from experimental data is more dependent on using potential function rather than the EoS. The results show that MPTA-Steele method is more appropriate for associating systems, due to considering appropriate molecular interactions.

By comparing the results for different cases, it is found that SRK EoS has a great compatibility with MPTA model, even for associating systems with polar adsorbents; the results are competitive with those obtained by CPA EoS. It can be concluded that using a sophisticated EoS does not necessarily improve the accuracy of the modeling, while it seems that suggesting a proper EoS highly depends on the type of the adsorbent and adsorbate. Our calculations have shown that the type of adsorbent and adsorbate can have a great influence on the results. Meanwhile it is worth mentioning that utilizing a cubic EoS can improve the convergence speed of equilibrium calculations.

Acknowledgments The authors appreciate precious assistance from Professor Alexander A. Shapiro and wish to acknowledge his hints and co-operation.

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