

# An efficient algorithm for modeling the thermodynamics of multi-solute adsorption from liquids



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## ABSTRACT

We propose a simple but very efficient method for the modeling of the multi-solute adsorption from liquids. The thermodynamic model used is an extension of a classical model for non-ideal multi-solute adsorption in the solid phase for binary and ternary solute systems. An algorithm is proposed for the solution of the constitutive equations that allows for the flexibility of the originally constant parameters involved in the equations correlating the Gibbs energy with composition in the solid phase. Using our own experimental data for the adsorption of paraxylene, metaxylene and ethylbenzene on BaX zeolite, the method is tested for binary and ternary solute systems using isooctane as solvent. The model is able to predict the separation factors of the binary and ternary solutes adsorption systems with a high accuracy.

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## 1. Introduction

The thermodynamics of multi-solute adsorption is an old subject and has been extensively studied over the past 70 years. Despite its industrial importance, liquid phase adsorption has been overshadowed by gas phase adsorption during this time span. The very first approach of Myers and Prausnitz [1] in modeling the thermodynamics of mixed gas adsorption was considered by Radke and Prausnitz [2] to describe multi-solute adsorption from dilute liquid solutions with the solid phase behaving ideally. The latter authors borrowed the concept of ‘invariant adsorption’ of solutes based on the Gibbs surface excess quantities [3]. Radke and Prausnitz [2] presented a rigorous theoretical description of the multi-solute adsorption phenomenon with minimum assumptions. However, they declared in their paper that their method could be of limited usefulness in the case of high solute concentration due to non-ideal behavior of the adsorbed phase. This problem was tackled afterwards by Minka and Myers [4], whose method soon became the basis of most of the later investigations on non-ideal solid phase multi-solute adsorption. Minka and Myers [4] applied the concept of surface excess property, a quantity directly measured experimentally. Their thermodynamic treatment required the calculation of derivatives of the excess free energy as a function of composition, and this

could be a source of error [5]. To describe ternary solute systems, methods based on surface excess need exact data regarding each pair of two-solute adsorption isotherms. In other words, they make the assumption that the excess free energy for a ternary system is simply the sum of the excess free energies of the constituent binaries [5]. This methodology has not shown satisfaction in predicting ternary solutes C<sub>8</sub> aromatics adsorption on Faujasite zeolites [5]. Price and Danner [6] tried to couple the method of Minka and Myers [4] with the kinetic approach of the adsorption from liquid phase onto homogeneous solids of Dąbrowski [7], obtaining more reasonable agreement between model and experimental results. Improvement to the parameter estimation procedure of the latter has been reported by Tourani et al. [8], who applied a neural network to obtain the optimum parameters of the excess Gibbs energy model based on the experimental data of Tournier et al. [9]. Statistical methods have proved useful in modeling multi-solute adsorption from liquids [5]. Monsalvo and Shapiro [10] presented a model based on the multi-component potential theory of adsorption (MPTA model). The same authors claimed that the MPTA model needs further improvements, like combination with more theoretically sound equation of states. However, they are subject to some criticism regarding the assumptions taken.

After this short introduction, we introduce the aim of the present work. We propose a simple but very efficient algorithm for the modeling of the multi-solute adsorption from liquids concentrating on the non-ideal behavior of the solid phase. The thermodynamic model used is an extension of the model of Radke

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## Nomenclature

$\mu$	Chemical potential (J mole <sup>-1</sup> )
$G$	Gibbs energy (J mole <sup>-1</sup> )
$\pi$	Spreading pressure (N m <sup>-1</sup> )
$n$	amount of adsorption (mol)
$T$	Temperature (K)
$R$	Universal gas constant (J mole <sup>-1</sup> K <sup>-1</sup> )
$x$	Fractional concentration in the solution (dimensionless)
$z$	Fractional concentration in the solid (dimensionless)
$Z$	Parameter defined in Eq. (15)
$\gamma$	Activity coefficient (dimensionless)
$c$	Concentration (mol l <sup>-1</sup> )
$A^*$	Adsorbent surface area (m <sup>2</sup> )
$A, B, C$	Parameters defined in Eqs. (10)–(15)

### Subscripts and superscripts

$i$	Component $i$
$0$	Standard state
$a$	Adsorbed state
$l$	Liquid phase
$m$	Invariant adsorption state
$T$	Total
$E$	Excess property

and Prausnitz [2] to non-ideal multi-solute adsorption in the solid phase for binary and ternary solute systems. An algorithm is proposed for the solution of the constitutive equations that allows for the flexibility of the originally constant parameters involved in the equations correlating the Gibbs energy with composition in the solid phase. The methodology used resembles to a great extent the modeling of the kinetics of dynamic systems making use of a pseudo-steady state assumption for each experimental point (time). It should be mentioned that several researches have provided experimental data for the mixed xylene–ethylbenzene systems using different solvents [11–13]. Using our own experimental data for the adsorption of paraxylene, metaxylene and ethylbenzene on BaX zeolite using isooctane as solvent, the method is applied for the prediction of binary and ternary solute system's thermodynamic equilibrium. The efficacy of the model in accurately predicting the separation factors of the binary and ternary solutes adsorption systems is discussed. We make use of our own adsorption data taken in our laboratory based on the ATR–FTIR technique. Accordingly, the first part of Section 3 describes the experimental isotherms obtained.

## 2. Experimental

Commercial BaX zeolite agglomerate (SPX-3003, CECA) has been used. Reagent grade xylene isomers (para and meta), ethylbenzene and isooctane were purchased from Loba Chemie.

Adsorption experiments were performed by the following procedure: (1) 1 g BaX zeolite was placed in a glass container and heated for 2 h at 250 °C in an electrical furnace to reach the required water content of ca. 4 wt.% (according to Minceva and Rodrigues [13]). This amount of moisture was obtained using a special calibration curve based on the weight loss of the initial zeolite when placed for different amounts of time in an electrical furnace. (2) The hot glass container was closed with a rubber cap and punched with an aluminum ring immediately after being taken out from the furnace. This procedure inhibits water adsorption from the ambient. (3) The glass container was placed

in a dessicator to cool down. (4) The organic solution of predetermined composition was injected into the container. (5) The glass container was placed in a shaker-incubator with an agitation rate of 200 rpm at 20 °C and the adsorption process was continued for 6 consecutive days.

The initial composition of the liquid phase has always been very dilute concerning the xylene or ethylbenzene species, i.e., the concentration of isooctane was equal or larger than 96 vol.%. Accordingly, the liquid phase could be considered to behave ideally throughout the composition range under study. In each experiment, 1 g zeolite was put into contact with 5 cm<sup>3</sup> organic solution.

The concentration of the liquid phase after reaching the thermodynamic equilibrium has been measured using ATR–FTIR analytical technique. About 200  $\mu$ l samples were used for each of the ATR–FTIR studies.

A Thermal Nicolet Nexus 670 apparatus has been used with a ZnSe crystal. This technique allows a high analytical precision. The integrated area of the peaks centered at 1363, 794, 690 and 696 cm<sup>-1</sup> were considered for isooctane, paraxylene, metaxylene and ethylbenzene, respectively. In all cases, the background was excluded numerically before the evaluation of the integrated peak intensity. In the case of the peak overlapping when working with ternary solute systems, deconvolution was performed by a code written in purpose using MATLAB software. The analytical method used possesses a high degree of reproducibility allowing for a detection error of less than 0.001% within the compositional range under study. The reproducibility error of the adsorption experiments has been measured to be less than 1.5%.

## 3. Results and discussion

### 3.1. Experimental adsorption experiments

Fig. 1 and its insets show the typical ATR–FTIR spectrum of the liquid state for the ternary solute system under study (paraxylene 0.02954, metaxylene 0.04621 and ethylbenzene 0.04309 volume fraction, respectively). In the case of overlapping of the characteristic peaks (metaxylene and ethylbenzene), peak area determination has been performed through deconvolution of the multimodal curve. Fig. 2 shows the single solute/solvent calibration curves obtained for the volume range of 1–4 vol.% of the solute species (paraxylene, metaxylene and ethylbenzene). The reproducibility is high, as in most of the cases the error bars on the curves are not discernible. The coefficient of determination ( $R^2$ ) between the experimental data and the straight calibration lines is larger than 0.999 in all the cases. The technique used is thus very robust.

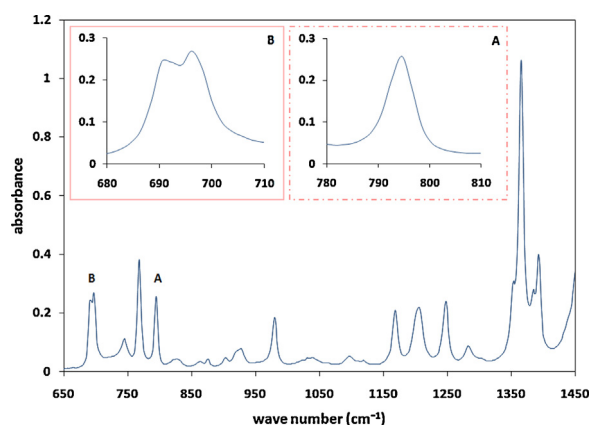


Fig. 1. A typical ATR–FTIR spectrum of the liquid state for the ternary solute system under study (paraxylene 0.02954, metaxylene 0.04621 and ethylbenzene 0.04309 volume fraction and isooctane 0.88116, respectively).

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