

Notes

On the Correlation of Modified Antoine's Adsorption Isotherm Models with Experimental Data

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Modified Antoine's adsorption isotherm models in various forms^{1–4} possess an adequate capability of describing vapor adsorption equilibria and predicting derived properties such as the Henry's law constant and the isosteric heat of adsorption within satisfactory agreement compared to other well-established models.⁴ The modified Antoine's adsorption isotherm can be expressed in several forms.^{1–3} The form considered in this note is given by

$$\ln(P) = A + \ln(\theta) - \frac{B + b(1 - \theta)}{T + C + c(1 - \theta)} = [A_c + \ln(P_c)] + \ln(\theta) - \frac{B + b(1 - \theta)}{T + C + c(1 - \theta)} \quad (1)$$

where P and P_c are the equilibrium and critical pressures, $A (=A_c + \ln(P_c))$, B and C are the original Antoine's equation parameters, b and c are correction factors for fractional surface coverage,⁴ $\theta (=n/m)$ is the fractional surface coverage, and n and m are the amount adsorbed and the saturation limit, respectively. A or A_c is chosen according to the form of the Antoine's equation (i.e., whether the critical pressure is included or not).

An expression for the Henry's law constant, K , can be derived from eq 1 with the result expressed as⁴

$$K = \left[\lim_{\theta \rightarrow 0} \left(\frac{P}{\theta} \right) \right]^{-1} = \frac{1}{P_c} \exp \left(\frac{B + b}{T + C + c} - A_c \right) = \exp \left(\frac{B + b}{T + C + c} - A \right) \quad (2)$$

Although Equation 2 appears to be independent of m , its effects are indirectly reflected in parameters b and c . Moreover, for a given pore volume, the saturation limit, m , is directly proportional to the adsorbed-phase density, which, in turn, can be either approximated from the liquid-phase density at the pure component VLE dew point temperature corresponding to the adsorption equilibrium pressure² or fitted from the experimental adsorption

Table 1. AREs^a in the Correlated Adsorption Equilibrium Pressures on Nuxite-AL Activated Carbon for the MA,⁴ MA1,² MA2, and RMA⁴ Models

compound	MA	MA1 ^b	MA2	RMA
CH ₄	3.44	6.11	2.79	2.68
C ₂ H ₄	5.07	5.73	4.68	4.44
C ₂ H ₆	5.30	6.14	4.69	4.53
C ₃ H ₆	19.55	9.60	15.82	12.56
C ₃ H ₈	17.64	10.44	15.29	9.22
C ₄ H ₁₀	28.15	23.55	27.46	26.30
CO ₂	13.56	14.34	11.91	10.81
av	13.24	10.84	11.81	10.08

^a ARE(%) = $(100/N) \sum_{i=1}^N (|P_i^{corr} - P_i^{exp}|/P_i^{exp})$; where N is the number of experimental data points in each data set and the superscripts "corr" and "exp" refer to the correlated and experimental adsorption equilibrium pressures, respectively. ^b Liquid phase densities are estimated for all the hydrocarbons at the appropriate temperatures using correlations in ref 2. The molar density of liquid CO₂ as a function of temperature is obtained from ref 7.

equilibria.⁴ The adsorbed-phase density is also temperature dependent and thus can vary with the adsorption conditions. In previous work,⁴ the temperature dependence of m was ignored in a modified form of the Antoine's adsorption isotherm model (denoted as MA). In the same work, a remodified Antoine's (RMA) adsorption isotherm model⁴ accounted for simple temperature dependencies in the model parameters, including m . RMA was shown to be superior to MA in both its correlative ability and predicting reasonable values of K , especially for the heavier components. However, it is shown below that the difference in these two models was mainly due to the choice of the objective function, but with a contribution also coming from ignoring the temperature dependence of the adsorbed-phase density. To make this point very clear, two other modified Antoine's adsorption isotherm models that account for the temperature dependence of the adsorbed-phase density in different ways are contrasted here against the MA and RMA models.

A model denoted here as MA1 accounts for the temperature dependence of the adsorbed-phase density by approximating it from the liquid-phase density in terms of a cubic function of temperature as done elsewhere.² Another option is to empirically correlate only the temperature dependence of m with the experimental adsorption equilibria using the same two-parameter exponential temperature dependence of m as in the RMA model.⁴ This later option, which is referred to as the MA2 model, isolates the effect of temperature on m (and hence the adsorbed-phase density) and is thus mathematically similar to the MA1 model² but different from the RMA model⁴ because it does not account for the temperature dependence of b and c . In this way, all four approaches, i.e., the MA,⁴ MA1,² MA2, and RMA⁴ models can be contrasted against each other with all but the MA model accounting for the temperature dependence of the adsorbed-phase density in one form or another.

Table 1 shows the average relative errors (AREs) in correlating the adsorption equilibrium pressures of various

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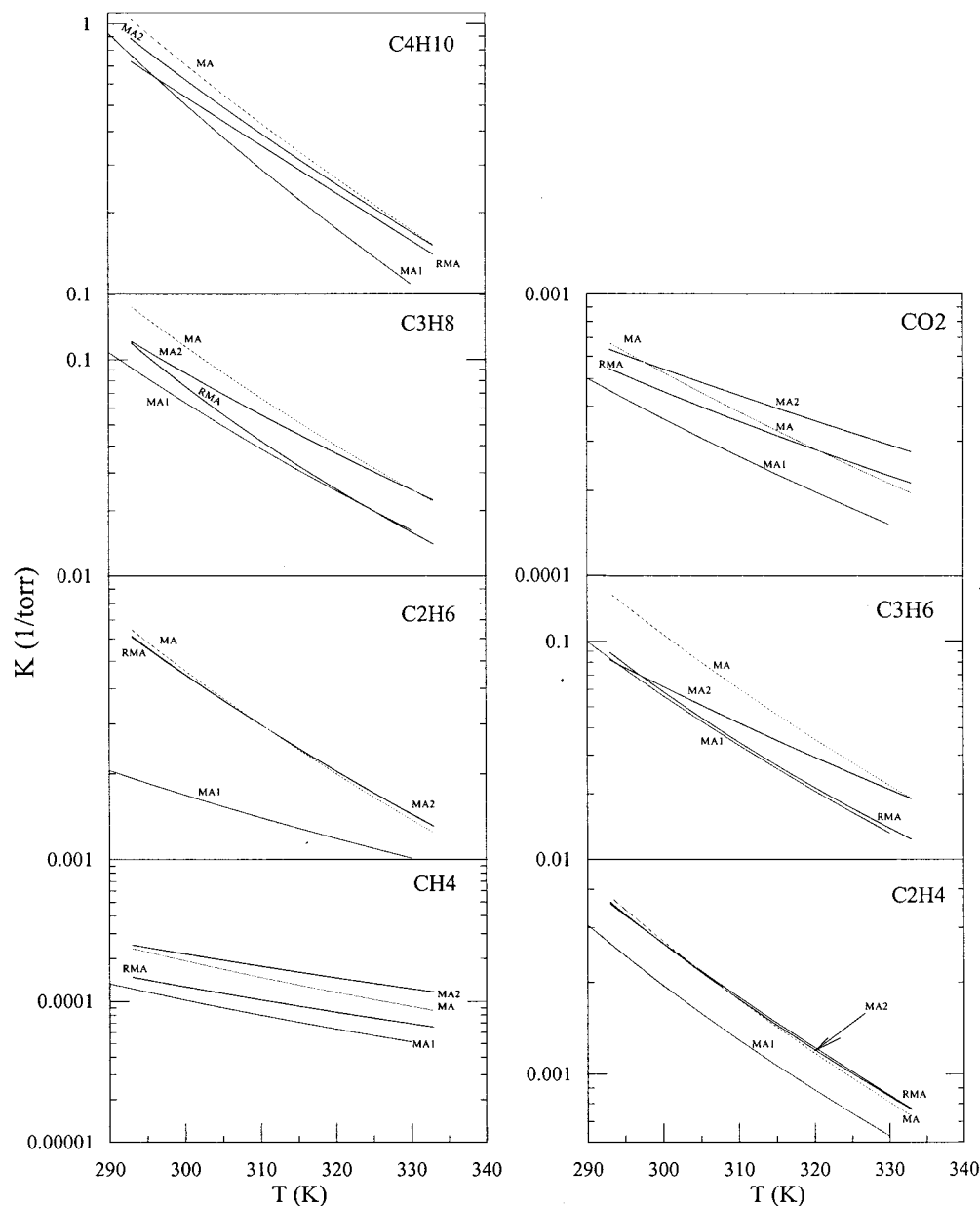


Figure 1. Predicted Henry's law constants from the MA,⁴ MA1,² MA2, and RMA⁴ models as a function of temperature for different adsorbates on Nuxite-AL activated carbon.^{5,6}

adsorbates on Nuxite-AL activated carbon^{5,6} using the MA, MA1, MA2, and RMA models. These fits were all optimized by using the least sum square error (LSSE) in $\ln(P)$. As might be expected, the accuracy of fitting the adsorption equilibria with the MA2 model was slightly better than that with the MA model (with temperature-independent m),⁴ and it even approaches the accuracy of the RMA model. It is important to point out, however, that the AREs from the MA and RMA models shown here are less than those presented previously⁴ because of changing the objective function from the LSSE in P to the LSSE in $\ln(P)$. The major effect of improving the objective function is noticeable mainly in the Henry's law constants predicted from the MA model. These are shown in Figure 1, along with those obtained from the other three models.

The K s predicted from the MA model for low adsorption affinity conditions (for light components and at high

temperatures) fall within the same range as those from the other three models, as they did in the previous study.⁴ However, for heavy components (heavier than ethane), especially at low temperatures, they still suffer from overestimating the Henry's law constants, which is similar to, but not as deviant as, the results obtained from the MA model with the objective function based on the LSSE in P .⁴ This result suggests that including the temperature dependence of the adsorbed-phase density is more important for heavier adsorbates. Moreover, only minor improvements were obtained in the previously presented K s from the RMA model⁴ as a result of using the improved objective function, which again suggests that it is important to include the effect of temperature on the adsorbed-phase density. It is noteworthy that because the new objective function did not markedly improve the correlative ability of the RMA model, the effect on the isosteric heats of adsorption obtained from the RMA model and presented in the previous study⁴ was also minimal.

Ideally, the temperature dependence of the adsorbed-phase density (or alternatively m) should always be

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accounted for when using any version of this model. Not accounting for this temperature dependence, as demonstrated with the MA model, in several cases resulted in marked differences in both the correlative ability (Table 1) and predicting reasonable values of K (Figure 1) compared to the RMA model. These differences seem to be more pronounced at lower temperatures, where it is presumably more important to include the temperature dependence.

The results in Figure 1 also reveal that approximating the adsorbed-phase density from that of the liquid-phase density at the pure component VLE dew point temperature corresponding to the adsorption equilibrium pressure (MA1)² tends to predict smaller K s compared to fitting it from the experimental adsorption equilibria (MA2 and RMA). It is not possible, however, to state which approach provides more realistic predictions of the K s. Nevertheless, the results in Table 1 show that, except for MA, the other three models have similar and reasonably accurate overall correlative abilities, with RMA showing slightly better results for the lighter components and MA1 for heavier components. In that sense, it is not possible to state in absolute terms which of the various forms of the modified Antoine's adsorption isotherm considered here is the most physically relevant; all are described by eq 1 with allowance for different temperature dependencies, which

can be expected to exist for real systems. The improved correlative ability of the RMA model is obtained from its extensive description of the adsorption equilibria through a sufficient number of fitting parameters, and thus it can be expected to be the most adequate for the purpose of describing data accurately. This, however, requires that the experimental adsorption equilibria be available at a sufficient number of temperatures over the range of interest. If this is not the case, more attention should be paid to the less intensive models, such as the MA2 or the MA1 models. The MA1 model can be used even for a predictive description of the temperature dependence of the adsorbed-phase density.

In conclusion, it suffices to state that the temperature dependence of the adsorbed-phase density should be accounted for in modified Antoine's adsorption isotherm models, especially for heavy adsorbates. Nevertheless, the importance of accounting for the temperature effects on the adsorbed-phase density becomes secondary after the choice of the objective function applied to any of these models. It is shown here that major errors can result if the pressure is used in lieu of the pressure logarithm as the objective function.

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