Further Modification of the Antoine Equation for Correlation of Adsorption Equilibria

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Introduction

Adsorption equilibrium data and heats of adsorption are essential for the proper design and operation of adsorption processes. The conditions (temperature and partial pressure) where these data need to be determined depend greatly on the specific requirements of the system. For example, pressure swing adsorption (PSA) processes need equilibrium data over relatively narrow ranges of temperature, whereas temperature swing adsorption (TSA) processes require much wider temperatures ranges. Moreover, heats of adsorption are usually estimated from the temperature dependence of the adsorption isotherms. Therefore, correlations that are very sensitive to temperature over relatively wide ranges are essential to the design and operation of such processes.

Several models are available in the literature for describing the temperature dependence of gas adsorption equilibria. Most of these models depend on the Polanyi pore-filling concept to obtain an explicit temperature dependence.[1−3] Other models, such as the extended Langmuir (EL) and the analytical heterogeneous extended Langmuir (AHEL) models,[4] can also be used for describing the temperature dependence of adsorption equilibria. However, such loading-explicit models are not very promising for the estimation of properties such as the isosteric heat of adsorption, which require determining the partial pressure dependence on temperature at constant loading.[5,6] Even those isotherms that can be manipulated as pressure-explicit isotherms, such as the EL and AHEL isotherms, are known to lose much of their accuracy after such manipulation. Instead, other pressure-explicit models, such as the modified Antoine (MA)[7−10] and virial adsorption isotherms,[11−23] can be more usefully applied to predict the isosteric heat of adsorption because they are based solely on pressure-explicit correlations in terms of temperature and loading.

In this work, the MA adsorption isotherm[7−10] is improved by introducing empirical temperature dependencies to its fitted parameters. A theoretical basis for the remodified Antoine (RMA) model is given based on an analogy with the virial adsorption isotherm. The RMA model is also used to derive an analytic expression for the single-component isosteric heat of adsorption. The derived expressions for correlating single-component adsorption equilibria and predicting single-component isosteric heats of adsorption are tested against well-established data and models in the literature. Difficulties and unresolved issues associated with predicting derived thermodynamic quantities, such as the isosteric heat of adsorption, from well-correlated, temperature-dependent adsorption isotherm data are discussed.

Theory

The MA adsorption isotherm can be expressed in different alternative formulas;[7−10] an example is shown in eq 1,

$$\ln\left(\frac{P}{P_c}\right) = A + \ln(\theta) - \frac{B + b(1-\theta)}{T + C + c(1-\theta)} \qquad (1)$$

where P is the absolute pressure of the adsorbate in the gas phase, P_c is the critical pressure of the adsorbate, T is the absolute temperature, and A, B, and C are the Antoine equation parameters. The fractional surface coverage, θ, is given by

$$\theta = Q/Q_m \qquad (2)$$

where Q is the moles or volume adsorbed per unit mass of adsorbent and Q_m is the maximum amount adsorbed in moles or volume. The parameters b and c have been used as temperature-independent fitting parameters to correlate single-component isotherms.[7−10] In terms of the volume adsorbed and the pore filling model,[8,9] the parameter Q_m has been taken as the pore volume of the adsorbent, W_0, which necessarily requires some assumption about the density of the adsorbed phase.[8,9] As an alternative, Q_m can be assumed to be temperature-dependent and used as a fitting parameter as shown below.

In this work, the MA adsorption isotherm was remodified by introducing an empirical temperature dependency to three of the parameters, namely b, c, and Q_m. The RMA isotherm is still given by eqs 1 and 2, but now the temperature dependence of b, c, and Q_m is best described by the following relations:

$$b = b^{(0)} + b^{(1)}T \qquad (3)$$

$$c = c^{(0)} + c^{(1)}T \qquad (4)$$

$$Q_m = {Q_m}^{(0)} \exp({Q_m}^{(1)}T) \qquad (5)$$

where $b^{(0)}$, $b^{(1)}$, $c^{(0)}$, $c^{(1)}$, ${Q_m}^{(0)}$, and ${Q_m}^{(1)}$ are temperature-independent fitting parameters. The MA and RMA adsorption isotherms can also be expanded to approximate the first three adsorption virial coefficients,[11−23] as shown in eqs 6−8.

$$A_v = \ln\left(P_c \exp\left(\frac{-(T + C + c)(A + \ln({Q_m}^{-1})) + B + b}{T + C + c}\right)\right) \qquad (6)$$

$$B_v = \frac{a}{2}\left(\frac{Bc - b(T + C)}{(T + C + c)^2\, Q_m}\right) \qquad (7)$$

$$C_v = \frac{-2a^2}{3}\left(\frac{c(b(T + C) + Bc)}{(T + C + c)^3 {Q_m}^2}\right) \qquad (8)$$

A_v, B_v, and C_v are the first three adsorption virial coefficients, respectively, and a is the adsorbent-specific surface area. These

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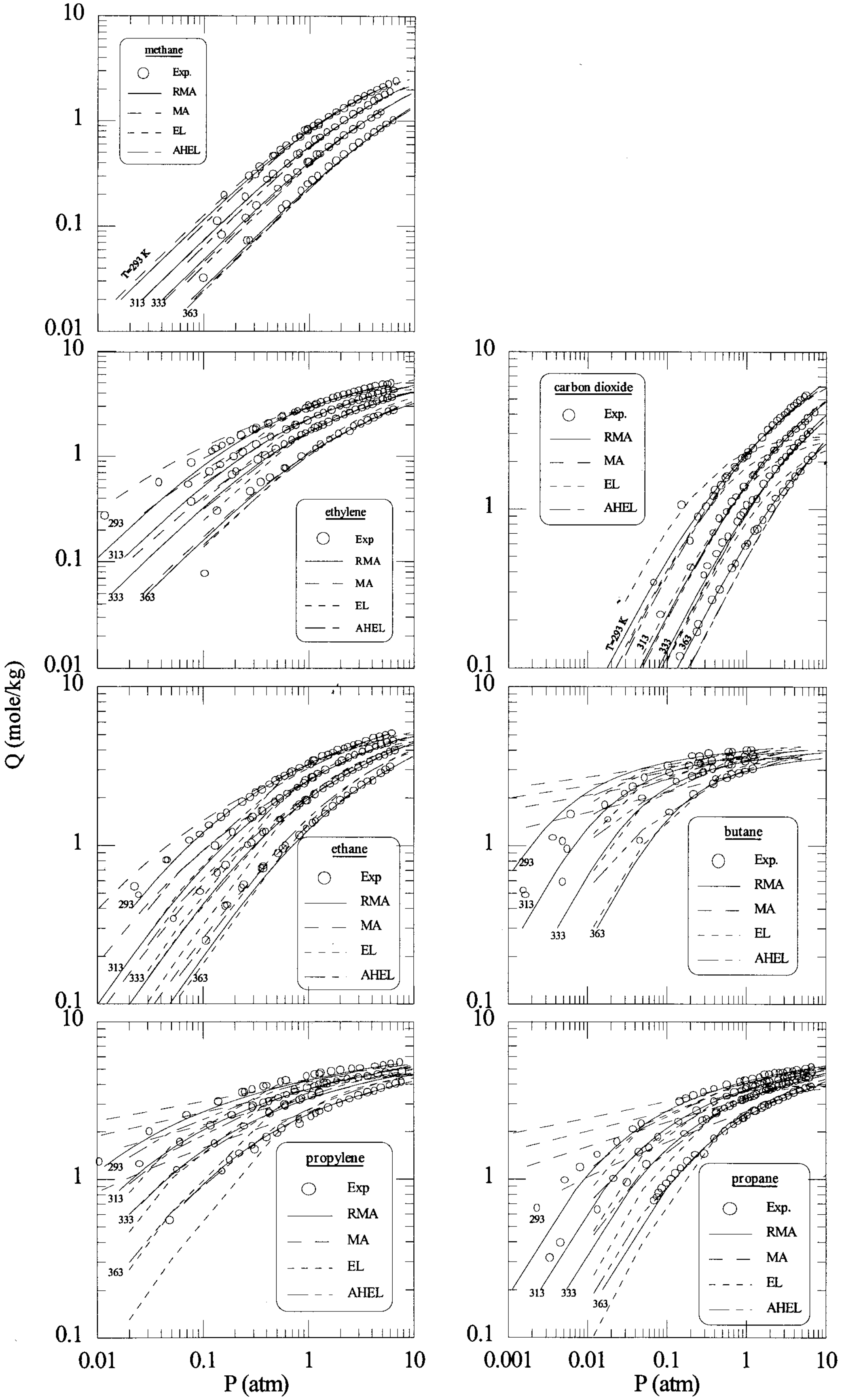

Figure 1. Single-component isotherm correlations from the MA, RMA, EL, and AHEL models for different adsorbates on Nuxite-AL-activated carbon.[28,29]

expressions show that the MA and RMA adsorption models, although originally based on a pore-filling concept when $Q_m = W_0$, can also be based on a two-dimensional virial description of adsorption equilibria with Q_m representing a two-dimensional

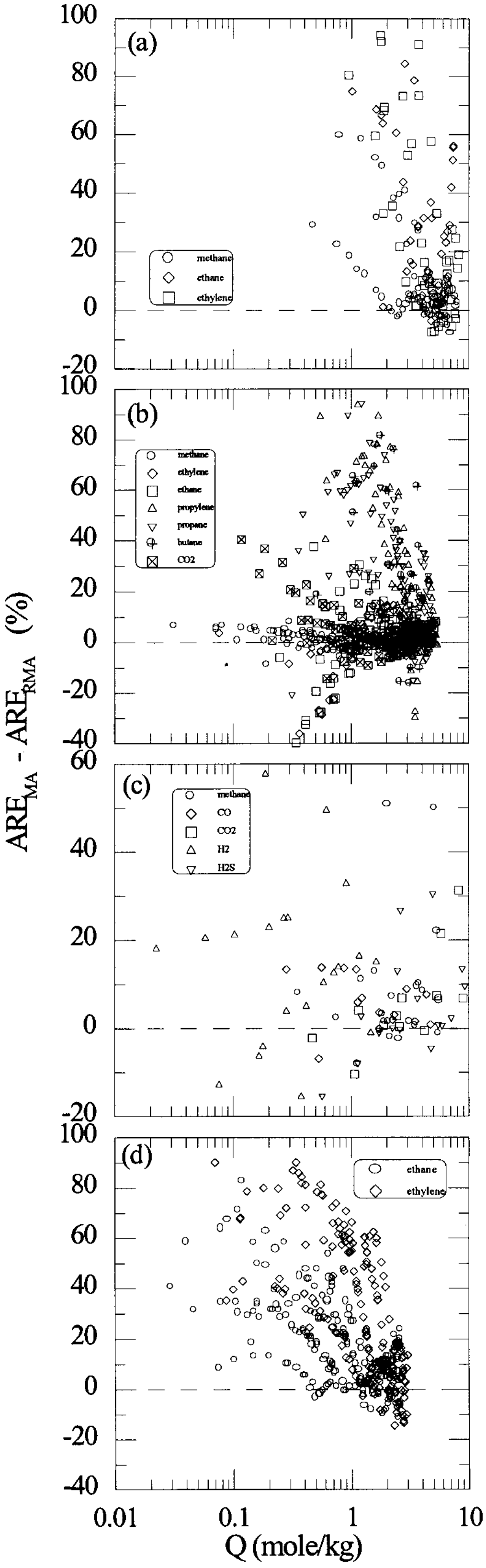

Figure 2. Difference between the AREs for the MA and RMA models for single gas adsorption on (a) BPL-activated carbon,[27] (b) Nuxite-AL-activated carbon,[28,29] (c) PCB-activated carbon,[30] and (d) 13X molecular sieve zeolite.[31−33]

saturation limit. The MA and RMA adsorption isotherms have a well-defined Henry's law constant, K, which is given by

$$K = \frac{1}{P_c}\exp\left(\frac{B+b}{T+C+c} - A\right) \tag{9}$$

where additional RMA temperature dependency is implicitly included in parameters b and c through eqs 3 and 4.

The isosteric heat of adsorption, q, is described by the Clausius−Clapeyron approximation as shown in eq 10.[5,6]

$$q = RT^2\left[\frac{\partial \ln P}{\partial T}\right]_Q \tag{10}$$

The subscript Q indicates that the amount adsorbed is held constant while taking the derivatives. The same relations can also be used when replacing the amount adsorbed with surface coverage.[8,24] Previous treatments[5,6] depended on replacing the pressure term in the above definitions by the amount adsorbed at both constant temperature and constant pressure by using the chain rule. Applying this definition to the MA and RMA isotherms gives the following expressions for the single-component isosteric heat of adsorption:

$$q^{\mathrm{MA}} = RT^2\,\frac{B + b(1-\theta)}{[T + C + c(1-\theta)]^2} \tag{11}$$

$$\mathrm{q}^{\mathrm{RMA}} = -RT^2\left(Q_{\mathrm{m}}^{(1)} + \frac{b^{(1)}(1-\theta) + bQ_{\mathrm{m}}^{(1)}\theta}{T + C + c(1-\theta)} + \frac{-(B + b(1-\theta))(c^{(1)}(1-\theta) + cQ_{\mathrm{m}}^{(1)}\theta + 1)}{(T + C + c(1-\theta))^2}\right) \tag{12}$$

Results and Discussion

Single-component adsorption isotherm systems were selected to cover a variety of adsorbates (hydrogen, methane, ethane, ethylene, propane, propylene, butane, carbon monoxide, carbon dioxide, and hydrogen sulfide) on four different adsorbents: (a) BPL-activated carbon, (b) Nuxite-AL-activated carbon, (c) PCB-activated carbon, and (d) 13X molecular sieve zeolite. The fixed properties of these adsorbates were obtained from the literature.[25] The EL and AHEL multicomponent adsorption isotherms[4] were selected for comparison with this new extension of the RMA adsorption model because of their simplicity and popularity, especially the EL model.[26] Based on a Langmuir form of temperature dependency, the EL isotherm is expressed as

$$Q_i = \frac{Q_{\mathrm{m}_i} b_i P_i}{1 + \sum_{j=1}^{N}(b_j P_j)} \tag{13}$$

$$b_j = b_{0_j}\exp\left(\frac{\epsilon_j}{RT}\right) \tag{14}$$

where Q_m, b_{0_j}, and ϵ_j are single-component fitting parameters obtained from eqs 13 and 14 with $N = 1$ and R is the universal gas constant. The AHEL isotherm is expressed

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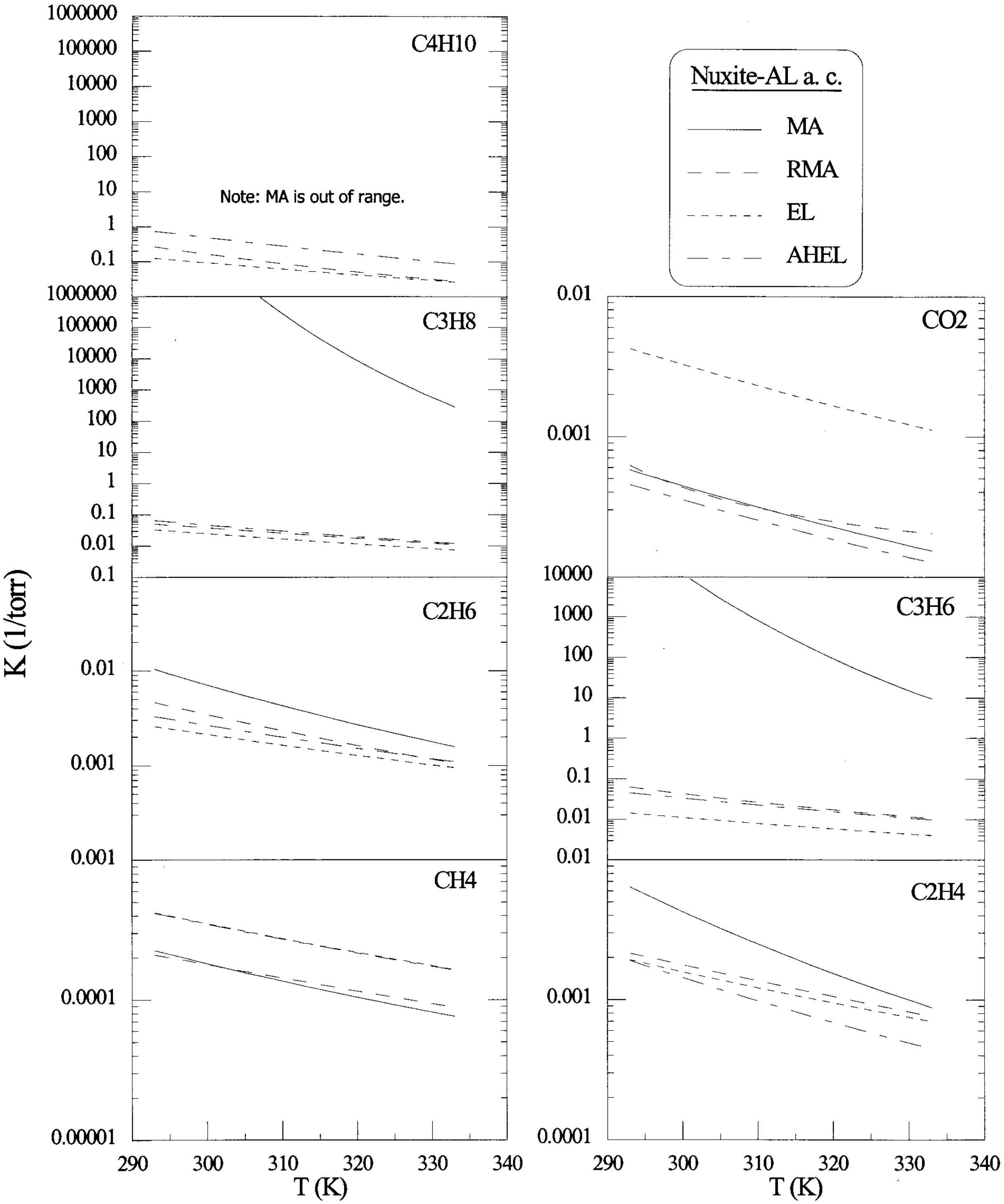

Figure 3. Predictions of the Henry's law constants from the MA, RMA, EL, and AHEL models as a function of temperature for different adsorbates on Nuxite-AL-activated carbon.[28,29]

in a temperature-dependent form of the UNILAN equation, as shown in eqs 15−19.

$$Q_i = \frac{Q_{m_i}\bar{b}_i P_i}{2\bar{s}\alpha} \ln\frac{1 + \alpha\exp(\bar{s})}{1 + \alpha\exp(-\bar{s})} \tag{15}$$

$$\alpha = \sum_{j=1}^{N} \bar{b}_j P_j \tag{16}$$

$$\bar{s} = \frac{1}{N}\sum_{j=1}^{N} s_j \tag{17}$$

$$\bar{b}_j = b_{0_j} \exp\left(\frac{\epsilon_j}{RT}\right) \tag{18}$$

$$s_j = 3^{1/2}\frac{\sigma_j}{RT} \tag{19}$$

where Q_m, b_{0_j}, ϵ_j, and σ_j are single-component fitting parameters obtained from eqs 15−19 with $N = 1$.

The MA and RMA models are both pressure-explicit;

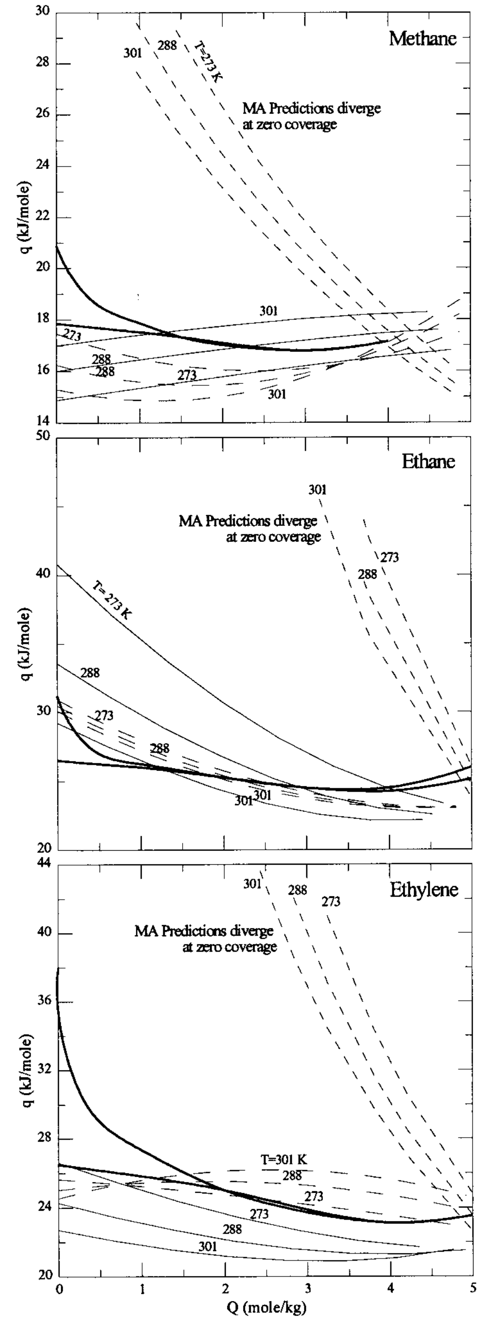

Figure 4. Predictions of the single-component isosteric heats of adsorption on BPL-activated carbon[27] from the RMA (solid thin lines), MA (dotted lines), and virial models (dashed lines),[11] compared with literature estimations (solid thick lines).[34]

thus, they were fitted to the data using the least-sum-squared error technique (LSSE) in predicting the equilibrium pressure for each adsorbent−adsorbate combination. For the MA model, the set of adsorption isotherms of each system was fitted simultaneously to eq 1 with b, c, and Q_m as the fitting parameters, with temperature dependency explicitly given by eq 1. A similar simultaneous procedure was followed by different investigators that studied the MA model,[7−10] but with $Q_m = W_0$. In contrast, for the RMA model, the set of adsorption isotherms of each system was again fitted simultaneously to eq 1 with $b^{(0)}$, $b^{(1)}$, $c^{(0)}$, $c^{(1)}$, $Q_m^{(0)}$, and $Q_m^{(1)}$ as the fitting parameters, so additional temperature dependence was given by eqs 3−5.

The EL and AHEL models are both loading-explicit; thus, they were fitted to the same data using the LSSE technique in predicting the equilibrium loadings for each adsorbent−adsorbate combination. These two models were also fitted simultaneously to the entire set of data associated with each system. In all cases, the “goodness” of the fit was judged in terms of the absolute relative error (ARE), defined as

$$\text{ARE} = \frac{(100\%)}{n}\sum_{i=1}^{n}\left[\frac{|P^{\text{exp}} - P^{\text{calc}}|}{P^{\text{exp}}}\right]_i \qquad (20)$$

where n is the total number of experimental data points.

Table 1 shows that the AREs of the RMA-correlated single-component adsorption isotherms were, in most cases, equivalent to or better than those of the AHEL model, which were remarkably better than those of the EL model. The correlations were noticeably more accurate, however, for the lightly adsorbed components. In most cases, the RMA model also reduced the AREs to less than 50% of those of the MA model. Figure 1 shows that the MA model overestimates the amounts adsorbed of the heavy components at low pressures, whereas the RMA model correlated the entire range of experimental data with a higher degree of flexibility. Figure 2 shows that the reduction in the AREs sometimes reached 100% of the MA model. Clearly, the RMA model has an enhanced capability to fit single-component adsorption isotherms over a wider range of conditions than the MA model. Moreover, Figure 3 shows that the RMA model always yields reasonable estimates of the Henry’s law constant for different adsorbates and at different conditions, while the MA fails for components heavier than propylene and at low temperatures. In most cases, the Henry’s law constants estimated with the RMA model are in the same range as those of the EL and AHEL models. This result adds another advantage of the RMA model over the MA model.

Figures 4 and 5 show that the isosteric heats of adsorption on BPL- and PCB-activated carbons predicted from the RMA model (eq 12) compared reasonably well with those obtained by Al-Muhtaseb and Ritter[11] from a virial-type model and by Valenzuela and Myers[34] from applying the chain rule technique to the Toth and UNILAN models; and in most cases, the predictions were much more reasonable than those obtained from the MA model. Almost all of the predictions of the isosteric heats of adsorption from the RMA model fell within the same range as the reference values.[34] On the other hand, in most cases, the reference values[34] were always close to the isosteric heats of adsorption predicted from the RMA model at the average temperature. This result was not surprising, as the reference values[34] assume that the isosteric heat of adsorption is temperature-independent over small temperature ranges but then use all of the data, in most cases, at significantly different temperatures to estimate one representative value of the isosteric heat of adsorption. In most cases, the RMA and virial estimations[11] also exhibited close trends with similar and only moderate temperature dependencies of the isosteric heat of adsorp-

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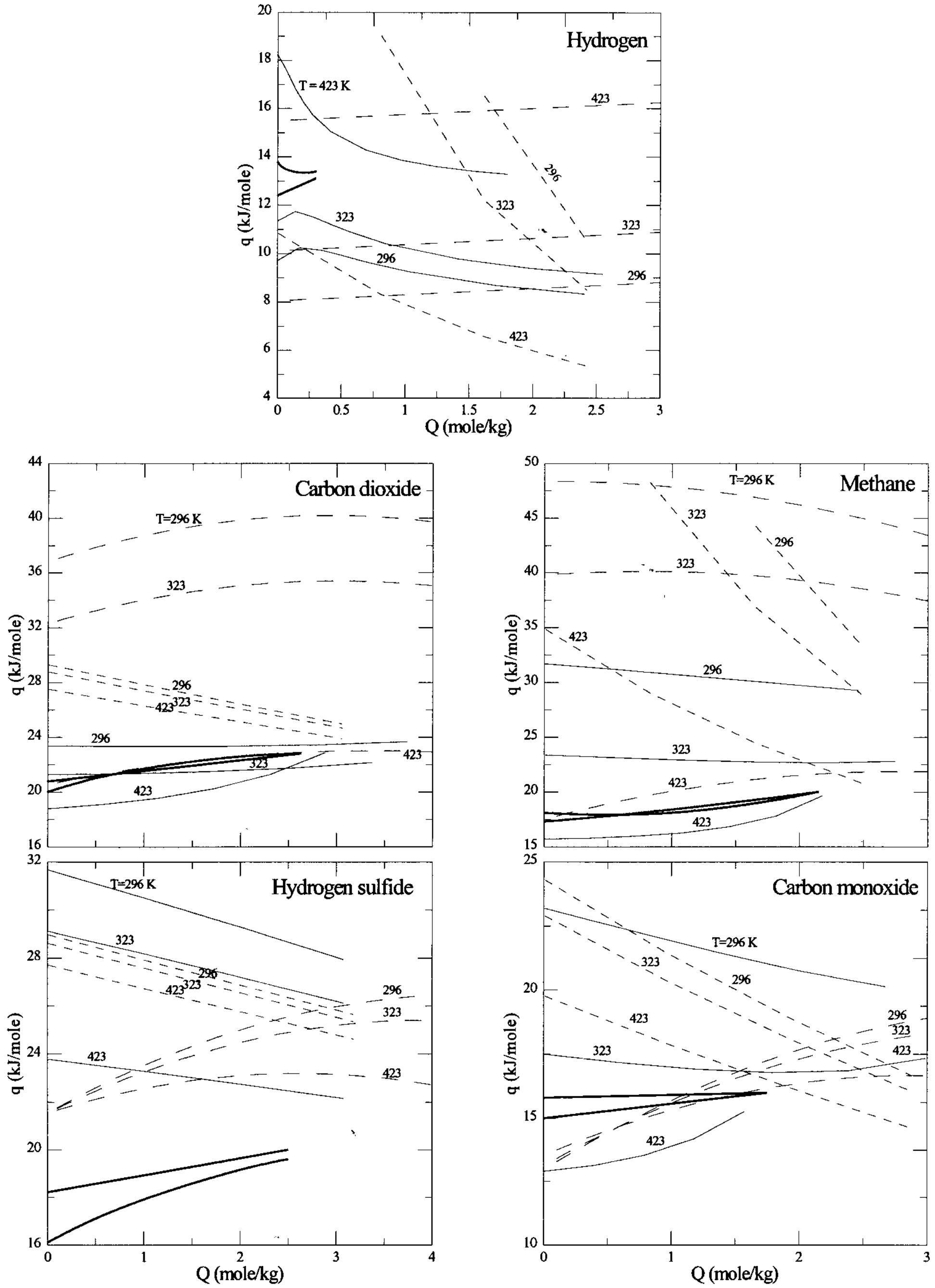

Figure 5. Predictions of the single-component isosteric heats of adsorption on PCB-activated carbon[30] from the RMA (solid thin lines), MA (dotted lines), and virial models (dashed lines),[11] compared with literature estimations (solid thick lines).[34]

Table 1. Comparison of the Single-Component Isotherm Data Sets Fitted to the Different Adsorption Models[a]

adsorbent	adsorbate	temp range (K)	ref	ARE^{MA} (%)	ARE^{RMA} (%)	ARE^{AHEL} (%)	ARE^{EL} (%)
BPL-activated carbon (a)	C_2H_6	213−301	27	43.11	18.66	16.48	71.06
	C_2H_4	213−301	27	32.73	8.93	11.55	67.92
	CH_4	213−301	27	16.77	6.86	6.13	53.44
Nuxite-AL-activated carbon (b)	C_4H_{10}	293−363	28	44.70	47.58	27.37	189.42
	CO_2	293−363	28,29	16.29	12.08	17.37	370.48
	C_2H_6	293−363	28,29	8.17	7.57	19.53	48.43
	C_2H_4	293−363	28,29	8.78	8.62	8.17	70.29
	CH_4	293−363	28,29	3.51	3.43	7.16	7.38
	C_3H_8	293−363	28,29	37.53	11.61	18.60	138.37
	C_3H_6	293−363	28,29	37.81	16.78	31.86	109.75
PCB-activated carbon (c)	CO_2	296−480	30	14.04	8.27	16.76	25.40
	CO	296−473	30	10.68	4.83	9.46	12.50
	H_2	296−480	30	22.39	7.65	11.37	11.19
	H_2S	296−480	30	12.15	9.60	8.39	37.16
	CH_4	296−480	30	16.29	7.13	12.34	14.91
13X molecular sieve zeolite (d)	C_2H_6	273−423	31−33	19.86	10.88	11.52	21.62
	C_2H_4	298−423	31−33	15.12	15.78	90.98	110.38

[a] ARE is defined by eq 20.

tion. This weak temperature dependence is in good agreement with the assertion that the isosteric heat of adsorption is independent of temperature over small temperature ranges. However, some deviations between the RMA and virial models were observed.

These discrepancies in the predictions from different models raise some interesting issues on the use of different models for the prediction of derived thermodynamic quantities such as the isosteric heat of adsorption, from well-correlated, temperature-dependent adsorption isotherm data. For example, although the RMA and virial[11] models correlated the temperature dependence of the adsorption isotherm data equally well, the same was not true for the temperature dependence of the isosteric heat of adsorption, especially at conditions or for systems that foster high adsorption affinity. The only plausible explanation for these discrepancies lies in the form of expressions used to represent the temperature dependence of the various adsorption isotherm parameters, e.g., those in eqs 3−5 for the RMA model. For the most part, these expressions are empirical and obtained only from experience in correlating isotherm data. Clearly, experimental evidence of the temperature dependence of the isosteric heat of adsorption for a variety of systems and conditions is needed to better quantify and understand the discrepancies between models. This is a greatly overlooked area of experimental research; and thus, only a paucity of information is available, which explains why the concept generally adopted by most investigators is that the isosteric heat of adsorption is temperature-independent. However, according to these results, this may be true only when dealing with experimental data over relatively narrow ranges of temperature.

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