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A Modified Pore-Filling Isotherm for Liquid-Phase Adsorption in Activated Carbon

S. Ismadji and S. K. Bhatia*

Department of Chemical Engineering, The University of Queensland, St. Lucia, QLD 4072, Brisbane, Australia

Received July 3, 2000. In Final Form: October 16, 2000

This article modifies the usual form of the Dubinin–Radushkevich pore-filling model for application to liquid-phase adsorption data, where large molecules are often involved. In such cases it is necessary to include the repulsive part of the energy in the micropores, which is accomplished here by relating the pore potential to the fluid–solid interaction potential. The model also considers the nonideality of the bulk liquid phase through the UNIFAC activity coefficient model, as well as structural heterogeneity of the carbon. For the latter the generalized adsorption integral is used while incorporating the pore-size distribution obtained by density functional theory analysis of argon adsorption data. The model is applied here to the interpretation of aqueous phase adsorption isotherms of three different esters on three commercial activated carbons. Excellent agreement between the model and experimental data is observed, and the fitted Lennard–Jones size parameter for the adsorbate–adsorbate interactions compares well with that estimated from known critical properties, supporting the modified approach. On the other hand, the model without consideration of bulk nonideality, or when using classical models of the characteristic energy, gives much poorer fits of the data and unrealistic parameter values.

1. Introduction

Activated carbon is one of the most important microporous adsorbents from an industrial view of point. Activated carbon has a very complex structure, with pore sizes ranging from micropores (<2 nm slitwidth) to macropores (>50 nm diameter), and has a variety of surface groups, impurities, and irregularities. Different preparation methods and precursors are used in its manufacture. The pore size, shape, and pore network connectivity of the activated carbon depend on the precursor used and the method of preparation, and strongly influence the adsorption process. Therefore, characterization of the pore structure of the activated carbons is crucial to adsorption and separation processes.

Several methods of analysis have been developed and applied for characterizing the pore structure of activated carbon, among which gas adsorption measurements are most commonly used. One of the most widely used isotherm equations in the characterization of pore structure and description of the micropore filling process in microporous adsorbents is the Dubinin–Radushkevich equation.^{1–7} The Dubinin–Radushkevich (DR) equation has a uniform general form that is useful for most adsorbates and follows the expression

$$\theta = \frac{q}{q_{\max}} = \exp\left[-\left(\frac{A}{\beta E_0}\right)^2\right] \quad (1)$$

where θ is fractional adsorption, q is the amount adsorbed, q_{\max} is the maximum capacity in the pore, whereas β and

E_0 are an affinity coefficient and characteristic energy, respectively. The adsorption potential, A , is usually expressed as

$$A = RT \ln\left(\frac{p_0}{p}\right) \quad (2)$$

here p_0 and p are the saturation pressure and equilibrium pressure, respectively. The Dubinin–Radushkevich equation can in principle be extended to liquid-phase adsorption⁸ by replacing the saturation and equilibrium pressures, p_0 and p , with the solute solubility C_s and the equilibrium concentration C_e , at given temperature T , respectively. Thus,

$$A = RT \ln\left(\frac{C_s}{C_e}\right) \quad (3)$$

Applications of the Dubinin–Radushkevich equation to liquid-phase adsorption are scarce because of complexities associated with other factors such as pH and ionic equilibria that are inherent in such systems. In addition, the solute–solvent interactions often render the bulk solution nonideal.

Theoretical studies of adsorption potentials between single molecules and model pores⁹ have shown that the characteristic energy, E_0 , is a function of the microporous structure of the activated carbon, and this has been related empirically to pore dimension by^{10,11}

$$E_0 = k/H \quad (4)$$

where k is a characteristic coefficient ($\approx 24 \text{ kJ}\cdot\text{nm}^{-1}\cdot\text{mol}^{-1}$)

* Corresponding author. E-mail: Sureshb@cheque.uq.edu.au.
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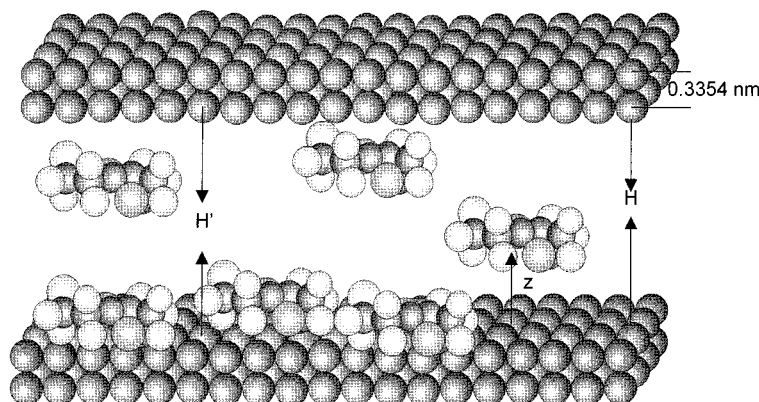


Figure 1. Model of carbon slit pore.

for benzene vapor in slitlike pores), and H is the width of slit pore. Other empirical forms of eq 4 have been developed and discussed extensively.^{12–14} These include McEnaney's relation¹²

$$H = 4.691 \exp(-0.0666E_0) \quad (5)$$

and that of Stoeckli et al.¹⁴

$$H = 30/E_0 + 5705/E_0^3 + 0.028E_0 - 1.49 \quad (6)$$

but there their relative accuracy has not been tested unequivocally. However, eq 4 and other related empirical forms such as those above are only approximate relations between the characteristic energy and pore width, and often cannot adequately describe the potential interaction between the adsorbate and adsorbent. In particular, when the molecular size approaches the pore width, the interaction becomes repulsive, a feature not captured in such approximations.

In this article a modified pore-filling model representing the characteristic energy in terms of the well-known Steele 10–4–3 potential,¹⁵ and thereby capturing the repulsive contribution to this energy is proposed. The model also incorporates the nonideality of the bulk liquid phase through the UNIFAC model. Experimental liquid-phase adsorption data were used to test the validity of the proposed model. Ethyl propionate, ethyl butyrate, and ethyl isovalerate were chosen as adsorbates, and three different commercial activated carbons Filtrasorb F-400, Norit ROW 0.8, and Norit ROX 0.8 were used as the adsorbents. Good agreement between the model and experimental data was observed, and the fitted parameters were consistent with expectation.

2. Model Formulation

The structural heterogeneity of activated carbon is generally characterized in terms of the pore-size distribution. The pore-size distribution represents a model of the internal structure of the solid, which assumes that an equivalent set of noninteracting and regularly shaped model pores can represent the complex void spaces within the real solid. The generalized adsorption isotherm (GAI)

equation is usually adopted for determination of the pore-size distribution, and has the following form

$$N(T, C) = \int_0^\infty q(T, C, H) f(H) dH \quad (7)$$

here $N(T, C)$ is the amount adsorbed per unit mass of adsorbent at temperature T and adsorptive concentration C , and $f(H)$ is the pore-volume distribution of the activated carbon. In actual application of eq 7 in fitting adsorption data it is beneficial to have independent characterization of the pore-size distribution $f(H)$, so that any unknown parameters are limited to the local isotherm $q(T, C, H)$. Lacking information on $f(H)$, this distribution is also often fitted in terms of an assumed form such as the gamma distribution.¹⁶ In this study, however, recourse to the latter has not been necessary, because argon isotherms for the carbons were measured and interpreted by means of density functional theory (DFT) to yield the pore-size distribution $f(H)$. The local adsorption isotherm $q(T, C, H)$ for micropores of width H is arbitrary, and the Dubinin–Radushkevich equation is chosen in our proposed model, leading to

$$N(T, C) = \int_0^{H_{\max}} q_{\max} \exp\left[-\left(\frac{A}{\beta E_0(H)}\right)^2\right] f(H) dH \quad (8)$$

where H_{\max} is a maximum micropore size. In the Dubinin–Radushkevich equation the maximum capacity, q_{\max} , has the following temperature dependence

$$q_{\max} = q_{\max}^0 \exp(\delta(T_0 - T)) \quad (9)$$

Here q_{\max}^0 is the maximum capacity at reference temperature T_0 (taken here as 303.15 K), and δ is a constant parameter representing the temperature coefficient of expansion of the adsorbate.

Because pores smaller than the critical dimension of the adsorbate molecules, d_c , are not accessible this value may be taken as the lower limit for the integration in eq 8. Such critical dimensions may be estimated by molecular simulation, as demonstrated in an earlier study.¹⁷ For the three esters used in this study, the values of d_c were obtained as 0.512 nm for ethyl propionate, 0.537 nm for ethyl butyrate, and 0.577 nm for ethyl isovalerate.¹⁷ The

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Table 1. Structural Characteristics of Activated Carbons Used

sorption characteristics	Filtrisorb-400	Norit ROW 0.8	Norit ROX 0.8
BET surface area (m ² /g)	877.82	849.39	978.85
micropore surface area (m ² /g)	761.8	718	847
micropore volume (cm ³ /g)	0.343	0.314	0.365
total pore volume (cm ³ /g)	0.468	0.443	0.467

total amount adsorbed may be now be expressed as

$$N(T, C) = \int_{d_c}^{H_{\max}} q_{\max}^0 \exp(\delta(T_0 - T)) \times \exp\left[-\left(\frac{A}{\beta E_0(H)}\right)^2\right] f(H) dH \quad (10)$$

As presented any arbitrary expression can be used for the adsorption potential A , and the characteristic energy E_0 in eq 10. Some classical formulations for these are given in eqs 2–6 but which, as discussed earlier, have numerous limitations. The crux of the present contribution is the use of an alternate formulation for the energy $\beta E_0(H)$ that includes repulsive contributions, and an improved expression for the adsorption potential A that accounts for bulk-phase nonideality. The latter is particularly important for liquid-phase adsorption. In this case large molecule adsorbates are also generally involved, for which the repulsive contribution to the pore-size-dependent energy also assumes significance and cannot be neglected. Our formulations for these are discussed in the subsequent sections.

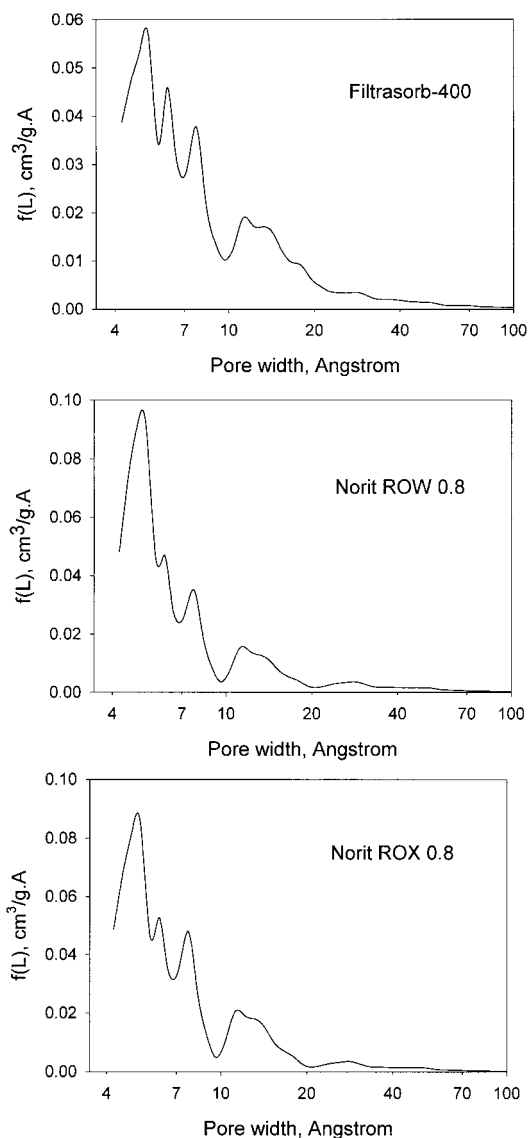
2.1. Characteristic Energy. For liquid-phase adsorption in micropores, as the bulk concentration of the adsorptive increases, the adsorbate will quickly start to fill the micropores, but the very narrow micropores can be filled only at high concentration because of a repulsive potential.¹⁸ Because the usual form, $\beta E_0(H) = \beta k/H$, in the Dubinin–Radushkevich (DR) equation does not include the repulsive interaction that is important at molecular scales, it loses accuracy at these scales. To alleviate this shortcoming it is proposed here to express the energy term $\beta E_0(H)$ in the terms of the fluid–solid interaction energy based on a Lennard–Jones model for intermolecular potentials. In this context Stoeckli and Morel¹⁹ proposed an empirical equation to correlate the characteristic energy with pore widths in terms of the fundamental fluid–solid interactions, which was revisited subsequently by McEnaney¹² to yield

$$\beta E_0(H) = \tau(\Omega - \Omega^\infty) \quad (11)$$

where τ is a constant, whereas Ω and Ω^∞ are the minimum potential in the micropore and the minimum potential on the flat surface, respectively. By using a statistical mechanical method, Chen and Yang⁶ also directly linked the characteristic energy of adsorption E_0 in the DR equation to the adsorption potential (Ω) in the pore, following

$$\beta E_0 = \Omega B N_0 \quad (12)$$

where B is a constant, and N_0 is the Avogadro number. Equation 12 of Chen and Yang has a form similar to that of eq 11, with the two approaching each other for very small pores for which $|\Omega| \gg |\Omega_0|$. At the other extreme of

**Figure 2.** Pore-size distributions of the activated carbons.

pore size, that is, $H \rightarrow \infty$, one may expect pore filling only as the adsorption potential $A \rightarrow 0$, leading to the condition $\beta E_0 \rightarrow 0$ as $H \rightarrow \infty$. This condition is satisfied by eq 11, but not by eq 12, suggesting wider applicability of the former. In this work we therefore use the expression in eq 11 for maximum flexibility. Although discussed earlier, this equation has never before been used for interpreting actual adsorption data or for characterizing carbons.

Clearly the term $(\Omega - \Omega^\infty)$ incorporates the repulsive interaction of large molecules in small pores²⁰ if a proper intermolecular potential model is used. The specification of the potential model for the molecular interactions in the system is therefore an important factor of the formulation in eq 11. It is well-established that the pores in activated carbon are slit-shaped; therefore, planar symmetry will be assumed. Based on this assumption, we use the 10–4–3 potential model of Steele,¹⁵ to describe the adsorption potential between the fluid molecules and the micropore wall, which is based on a Lennard–Jones intermolecular potential. In slit-shaped pores, for the interaction between an adsorbate molecule and a single extended pore wall, the Steele 10–4–3 potential model

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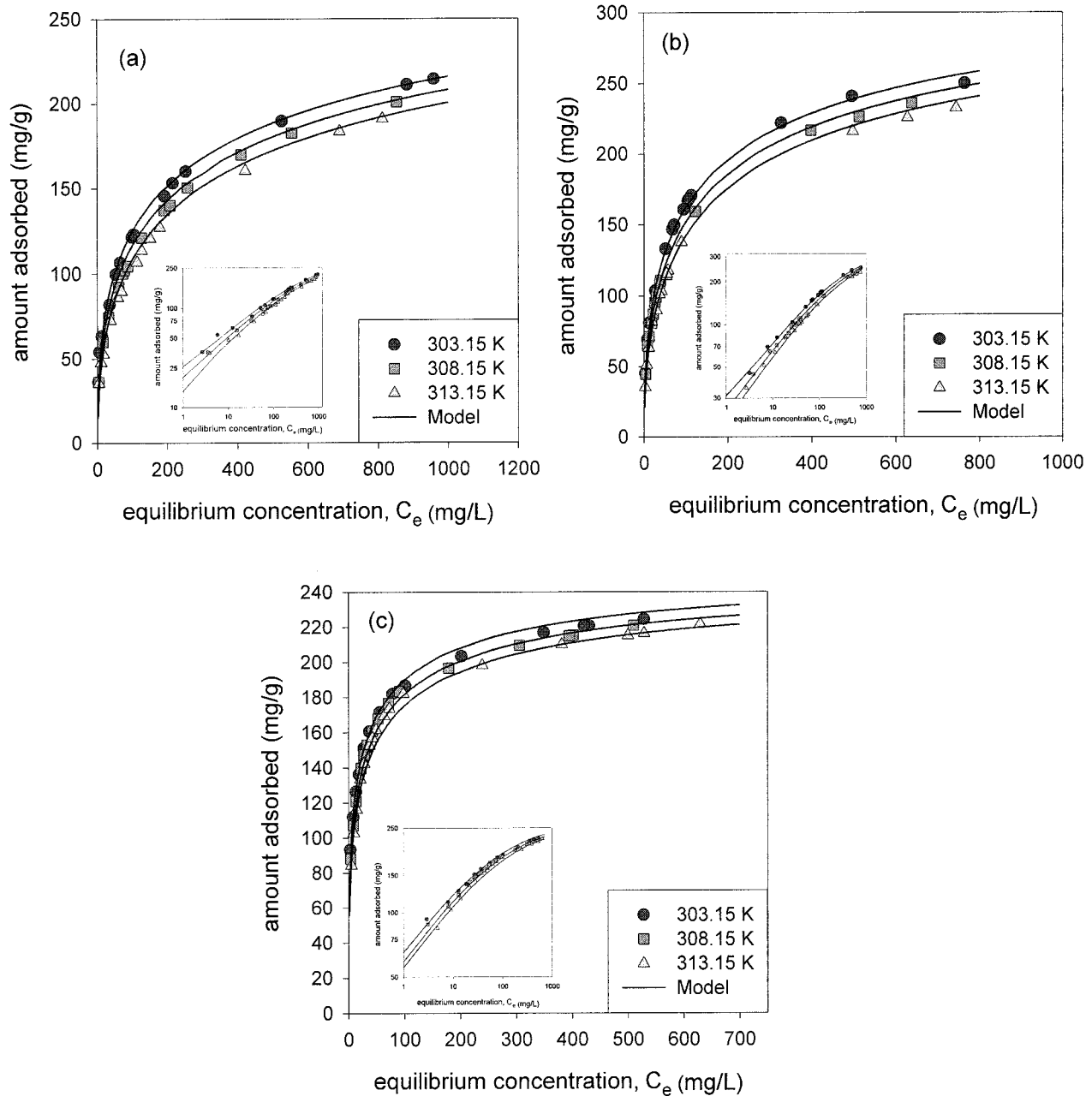


Figure 3. Experimental adsorption data and fit of model isotherm for (a) ethyl propionate, (b) ethyl butyrate, and (c) ethyl isovalerate on Filtrasorb 400 activated carbon.

has the form

$$\Phi_{CA}(z) = 2\pi\rho_c\epsilon_{CA}\sigma_{CA}^2\Delta\left[\frac{2\left(\frac{\sigma_{CA}}{z}\right)^{10}}{5} - \left(\frac{\sigma_{CA}}{z}\right)^4 - \left(\frac{\sigma_{CA}^4}{3\Delta(0.61\Delta + z)^3}\right)\right] \quad (13)$$

where z is the normal distance between an adsorbate molecule and the solid surface as shown in Figure 1, ρ_c is the solid density, and Δ is the interplanar distance of the graphitic sheets in carbon. These were taken as 114 nm^{-3} and 0.335 nm , respectively. The Lennard–Jones (LJ) parameters for the adsorbate–carbon interaction, ϵ_{CA} and σ_{CA} , were obtained using the classical Lorentz–Berthelot rules

$$\epsilon_{CA} = \sqrt{\epsilon_{CC}\epsilon_{AA}} \quad (14)$$

$$\sigma_{CA} = \frac{\sigma_{CC} + \sigma_{AA}}{2} \quad (15)$$

in which σ_{AA} is the LJ molecular size parameter, and ϵ_{AA} is the potential well depth for the adsorbate molecules. The LJ parameter values for carbon were taken from Steele and have the values $\epsilon_{CC}/k = 28.0 \text{ K}$ and $\sigma_{CC} = 0.3354 \text{ nm}$. The carbon micropore is idealized as a slit of width H (center-to-center distance between carbon atoms on opposing pore walls), which is infinite in both lateral directions. Consequently, there is a 10–4–3 potential contribution from each side of the slit, which provides the total pore potential

$$\Omega(z) = \Phi_{CA}(z) + \Phi_{CA}(H - z) \quad (16)$$

with $H = H + 0.3354$. Here H is the physical pore width. The minimum value of the adsorption potential of an adsorbate molecule is achieved at location z_{\min} , in terms

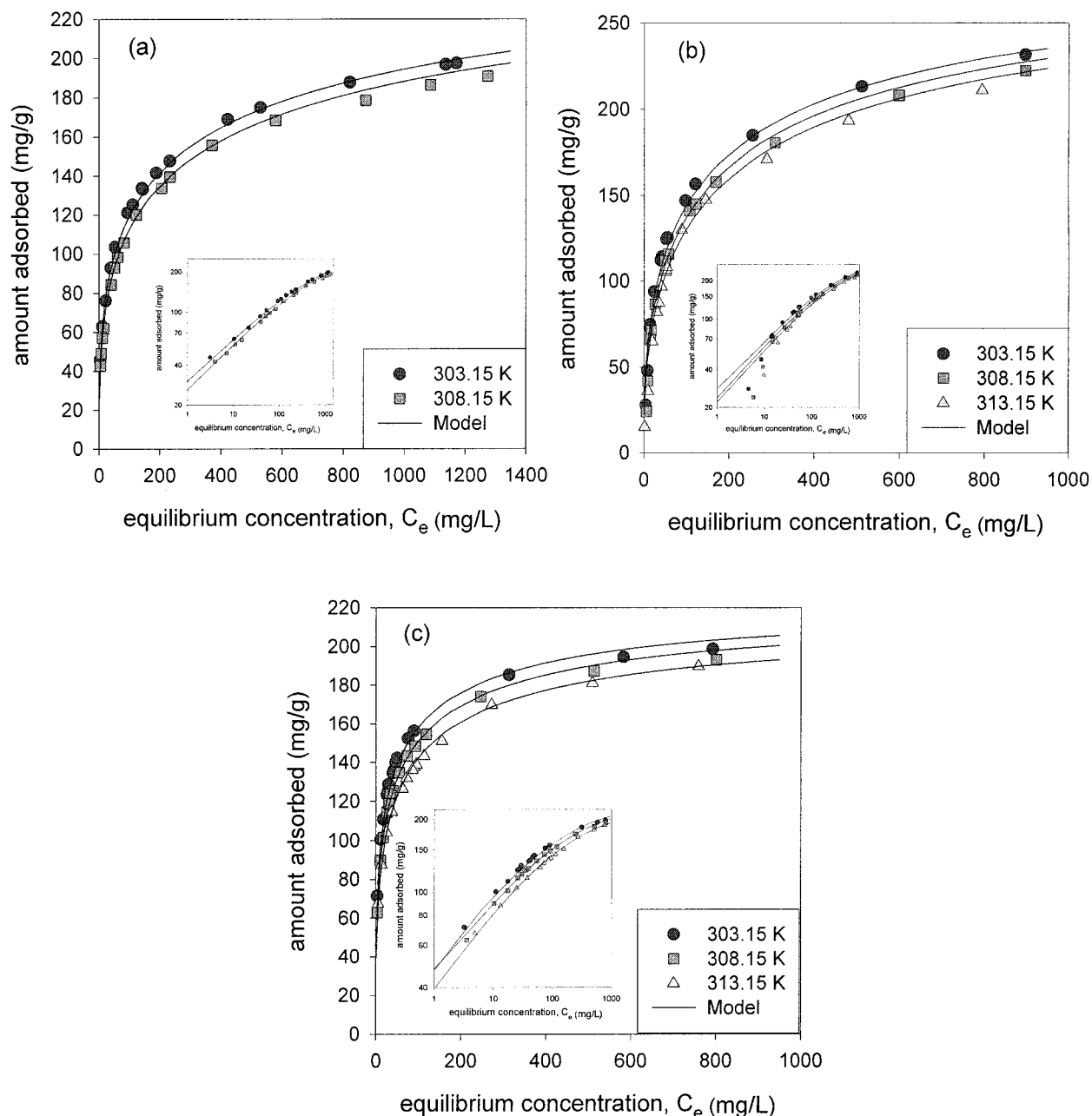


Figure 4. Experimental adsorption data and fit of model isotherm for (a) ethyl propionate, (b) ethyl butyrate, and (c) ethyl isovalerate on Norit ROW 0.8 activated carbon.

of which the minimum potential can be expressed as

$$\Omega(z_{\min}) = \Phi_{\text{CA}}(z_{\min}) - \Phi_{\text{CA}}(H - z_{\min}) \quad (17)$$

It may be noted that the Lennard–Jones interaction model above is generally accurate only for simple molecules such as Ar, N₂, and CH₄. However, our model additionally incorporates a second molecular dimension in terms of the critical size obtained by the molecular simulation, thereby improving the applicability of the LJ potential for more complex molecules. Any further deviations are embedded in the interaction parameter τ , which is a characteristic for a given adsorbate on carbon.

2.2. Nonideality of the Liquid Phase. The treatment of the nonideality of the bulk liquid phase is similar to that presented in our earlier work¹⁷ on characterization of carbon connectivity. However, for completeness and ready reference we briefly present the principal features.

In general the nonideality of the bulk liquid phase can be expressed through an activity coefficient for the liquid phase by the following equation:

$$\gamma_i^l(T, C_p, x) \equiv \frac{a_i}{x_i} = \frac{f_i^l}{x_i f_i^o} \quad (18)$$

where a_i is the activity of component i , f_i^l and f_i^o are the fugacity of ester in liquid mixture and fugacity of pure species, respectively. In the present model the concentration dependence of γ_i^l is expressed through the UNIFAC activity coefficient model²¹ which has the form:

$$\ln \gamma_i^l = \ln \gamma_i^l(\text{combinatorial}) + \ln \gamma_i^l(\text{residual}) \quad (19)$$

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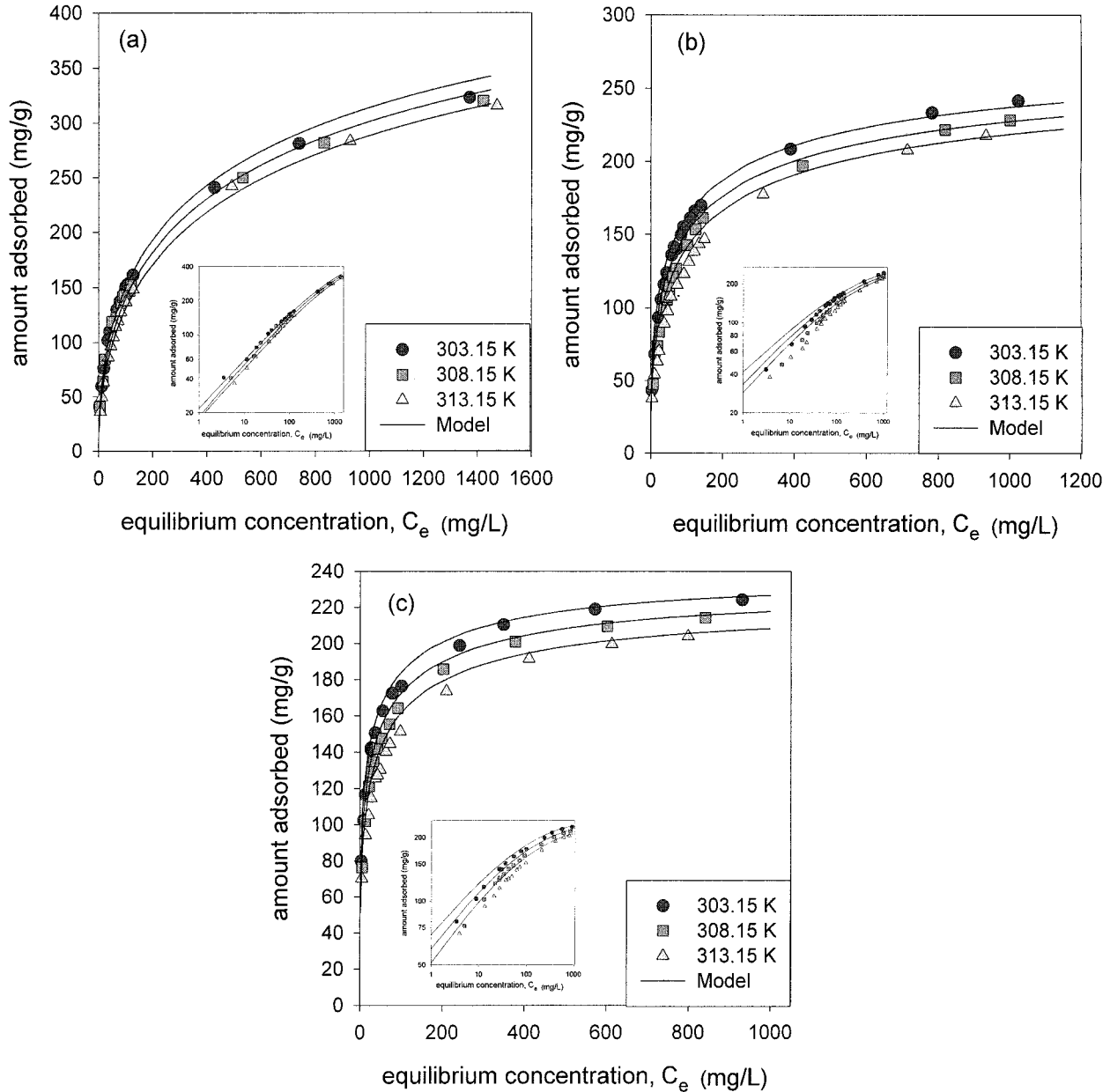


Figure 5. Experimental adsorption data and fit of model isotherm for (a) ethyl propionate, (b) ethyl butyrate, and (c) ethyl isovalerate on Norit ROX 0.8 activated carbon.

The combinatorial term in eq 10 is calculated using

$$\ln \gamma_i^l(\text{combinatorial}) = \ln \frac{\Phi_i}{x_i} + \frac{\xi}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_j x_j l_j \quad (20)$$

with $l_i = (r_i - q_i)\xi/2 - (r_i - 1)$. Here Φ_i is segment or volume fraction of species i , ξ is the average coordination number, usually taken to be 10, q_i , r_i , and θ_i are the surface area parameter, size parameter, and area fraction of species i , respectively. The residual term is evaluated by a group contribution method, so that the mixture is envisioned as being a mixture of functional groups, rather than of molecules.

$$\ln \gamma_i^l(\text{residual}) = \sum_k \nu_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \quad (21)$$

Here $\nu_k^{(i)}$ is the number of k groups present in the species

i , and Γ_k is the residual contribution to the activity coefficient of group k and can be defined as

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \Theta_m \Psi_{mk} \right) - \sum_m \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}} \right] \quad (22)$$

where Θ_m is surface area fraction of group m , and Ψ_{nm} is equal to $\exp(-a_{nm}/T)$ with a_{nm} as binary parameter for each pair of functional groups.

In the terms of the liquid-phase activities, eq 8 can be rewritten as

$$N(T, C) = \int_{d_c}^{H_{\max}} q_{\max}^0 \exp(\delta(T_0 - T)) \times \exp \left[- \left(\frac{RT \ln(a_s/a_e)}{\beta E_0(H)} \right)^2 \right] f(H) dH \quad (23)$$

where we used the general relation $A = RT \ln(a_s/a_e)$. Here

Table 2. Fitted Parameters of the Proposed Model Using DFT-Based Pore-Size Distribution

activated carbon and compound	q_{\max} (mg/cm ³)	σ_{AA} (nm)	τ	$\delta \times 10^3$ (K ⁻¹)	error, $E \times 10^2$ (mg ² /g ²)
Filtrosorb 400					
ethyl propionate	692.18	0.561	0.443	1.405	1.61
ethyl butyrate	770.49	0.588	0.362	2.416	0.98
ethyl isovalerate	665.61	0.649	0.408	3.369	0.59
Norit ROW 0.8					
ethyl propionate	745.14	0.578	0.438	1.397	1.24
ethyl butyrate	866.17	0.605	0.355	2.369	1.15
ethyl isovalerate	753.13	0.679	0.354	3.301	0.79
Norit ROX 0.8					
ethyl propionate	1050.77	0.577	0.378	2.361	0.58
ethyl butyrate	891.23	0.609	0.381	2.940	1.41
ethyl isovalerate	718.61	0.634	0.412	3.299	0.97

a_e and a_s are the activity of the adsorptive in the bulk liquid at saturation and equilibrium concentration, respectively.

Upon combining eqs 11, 17, and 23 we obtain the overall heterogeneous isotherm

$$N(T, C) = \int_{d_c}^{H_{\max}} q_{\max}^0 \exp(\delta(T_0 - T)) \times \exp\left[-\left(\frac{RT \ln(a_s/a_e)}{\tau(\Omega(H, z_{\min}) - \Omega^\infty(z_{\min}))}\right)^2\right] f(H) dH \quad (24)$$

that may be used in interpreting adsorption equilibrium data.

3. Experimental Section

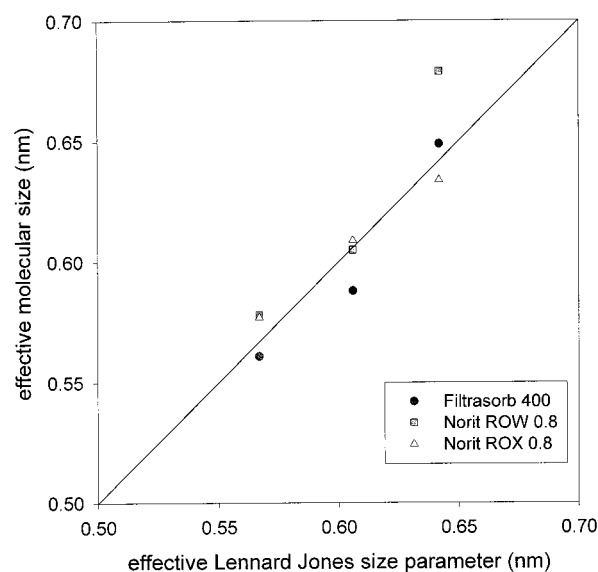
3.1. Materials. Three commercial activated carbons Filtrosorb 400, Norit ROW 0.8 (acid-washed), and Norit ROX 0.8 were used in this study. These carbons are food-grade-activated carbons and were obtained from Calgon Carbon. Before use, the fine particles of the activated carbon were removed by repeatedly washing with RO water and subsequently degassed under nitrogen flowing at 523.15 K for at least 16 h. The pore structure characteristics of the carbons [Brunauer–Emmett–Teller (adsorption isotherm) (BET) surface area, micropore surface area, micropore volume, total pore volume, and the pore-size distribution] were determined by argon adsorption at 87.15 K using an automatic Micromeritics ASAP-2010 volumetric sorption analyzer. Further details are discussed elsewhere,¹⁷ and the results summarized here in Table 1. The pore-size distributions of Filtrosorb 400, Norit ROW 0.8, and Norit ROX 0.8 obtained, based on argon adsorption using DFT with medium regularization are depicted in Figure 2. Bimodal pore-size distributions, with peaks around 0.45–0.55 nm and 1.4–1.6 nm for each activated carbon, are clearly evident in this figure.

The adsorbates used in this study were ethyl propionate, ethyl butyrate, and ethyl isovalerate. These adsorbates were obtained as analytical grade from Sigma Aldrich Pty., LTD (NSW, Australia) with purity of about 98–99%. The adsorbates investigated were used without further purification.

3.2. Adsorption Experiments. The adsorption experiments were performed isothermally in static mode at three different temperatures, 303.15, 308.15, and 313.15 K. In the adsorption experiments, known amounts of adsorbate were mixed with deionized water to yield various desired concentrations. Adsorption was performed on the carbons in a 250-mL flask placed in a controlled temperature water shaker bath (accurate to ± 0.1 °C). Equilibrium was attained within 24–48 h, and bulk concentrations determined by gas chromatography. Although concentration measurements were expected to be accurate within 1–2%, based on estimated calibration errors, the adsorbed amount data were reproducible within 10% at low concentrations and better at high values. Further details of the adsorption experiments can be found elsewhere.¹⁷

4. Results and Discussion

4.1. Isotherm Data and Model Application. Figures 3–5 present the experimental results for the adsorption

**Figure 6.** Correlation between effective molecular size and effective Lennard–Jones size.**Table 3. Accessible Pore Volume of Activated Carbons**

activated carbon and compound	accessible pore volume from	
	nonlinear fitting (cm ³ /g)	DR plot (cm ³ /g)
Filtrosorb 400		
ethyl propionate	0.316	0.310
ethyl butyrate	0.345	0.327
ethyl isovalerate	0.291	0.275
Norit ROW 0.8		
ethyl propionate	0.292	0.269
ethyl butyrate	0.323	0.259
ethyl isovalerate	0.266	0.228
Norit ROX 0.8		
ethyl propionate	0.455	0.426
ethyl butyrate	0.370	0.343
ethyl isovalerate	0.286	0.254

isotherms of three esters on different carbons at various temperatures. In these figures the experimental data are represented by symbols, and the solid lines are the model fits to be discussed here. These figures show that our proposed model describes the equilibrium adsorption data fairly well, although some deviation appears for Norit ROX 0.8 in the low-concentration region where relative data error can be larger (see the insets in Figure 5 using logarithmic coordinates). Interpretation of the data was performed by means of the model isotherm in eqs 13–17 and eq 24 by a nonlinear least-squares method. Because we use the DFT-based distribution in our model the fitting for each component was done separately, jointly using all the data at the different temperatures for the adsorbate

on a given carbon. For this purpose the sum of squared errors

$$E = \sum_i \sum_j (N(T_i, C_j) - N_{ij})^2 \quad (25)$$

was used as the objective function to be minimized. Here $N(T_i, C_j)$ is the predicted amount adsorbed, and N_{ij} is the experimental value, at temperature T_i and bulk concentration C_j . Such an objective function sacrifices accuracy at low concentrations in favor of higher concentrations, but this is justifiable in view of the larger data scatter in this region and the noted absence of a Henry's law asymptote for the Dubinin isotherm. The latter is considered to lead to deviations at low concentrations. Although this may cause the deviations at low concentrations seen in Figure 5, most likely the latter is due to specific oxidizing functionalities on this carbon that is an acid washed one.

For each ester on a given carbon the maximum capacity q_{\max} , interaction constant τ , effective molecular size σ_{AA} and the expansion coefficient δ were used as the fitting parameters. The value of ϵ_{AA}/k for each adsorbate was obtained by means of the well-known correlation²²

$$\epsilon_{AA}/k = 1.15 T_b \quad (26)$$

where T_b is normal boiling point of the adsorbate. The values of ϵ_{AA}/k for the three esters were obtained as 427.8 K for ethyl propionate, 451.9 K for ethyl butyrate, and 464.6 K for ethyl isovalerate. Table 2 presents the parameter values obtained from the isotherm fits. One of the good indications of the validity of the method is obtained from the values of the fitted effective molecular size, which are only slightly different from those estimated using a well-known correlation recommended by Reid et al.²²

$$\sigma = 0.809 V_c^{1/3} \quad (27)$$

that has a statistical mechanical basis. Here σ is the effective Lennard–Jones size parameter (Å), and V_c is the critical volume (cm³/mol). The value of the effective Lennard–Jones size parameter calculated from eq 27 was 0.567 nm for ethyl propionate, 0.606 nm for ethyl butyrate, and 0.642 nm for ethyl isovalerate. For all carbons the fitted effective molecular sizes increase with the corresponding effective Lennard–Jones size parameter, as expected. Figure 6 depicts the correlation between the fitted effective molecular sizes and effective Lennard–Jones size parameter for all three carbons studied, yielding consistent results.

It may be noted that in the IUPAC classification micropore widths are often assumed as being smaller than 2 nm. This is approximately valid for some small molecules such as nitrogen and carbon dioxide, and has prompted some workers²³ to consider the upper limit of the integration for the isotherm H_{\max} to be 2 nm. For the much larger ester molecules used here, which are almost twice as large, the upper limit for pore filling is considerably larger, and may be approximated by the statistical mechanical

correlation of Evans et al.²⁴

$$\frac{(T_c - T)}{T_c} = \frac{\lambda}{H_{\max}} \quad (28)$$

where T_c is the critical temperature and λ is the length scale of the adsorbate molecular interactions, taken as $2\sigma_{AA}$. This yielded H_{\max} in the range of 2.4–2.7 nm for the esters, but as seen in Figure 2 the DFT pore-size distributions show small pore volume beyond about 2 nm. This feature combined with the negligible adsorption potential of the larger pores made the results insensitive to H_{\max} larger than 2.4 nm, and for the calculations H_{\max} was therefore taken as infinity.

The accessible pore volume of the activated carbon can be determined from

$$V_{\text{acc}} = \frac{q_{\max}}{\rho_l} \int_{a_c}^{\infty} f(H) dH \quad (29)$$

where ρ_l is the liquid-phase density at the reference temperature of 303.15 K. The estimated values are summarized in Table 3, and correspond to those in pores larger than critical molecular size of each ester (0.512 nm for ethyl propionate, 0.537 nm for ethyl butyrate, and 0.577 nm for ethyl isovalerate). For comparison, the accessible pore volumes estimated from the DR plot, obtained from intersection of the DR characteristic lines with ordinate,¹⁷ are also summarized in Table 3. These results show that the accessible pore volume obtained from the nonlinear fitting procedure are slightly higher than those from the DR plot, with the difference ranging from 1.9 to 19.8% (predominantly below 10%). The deviation between the accessible pore volumes obtained from the two methods is understandable given the difference in the analysis methods used. Additionally, in the characteristic DR plot the variation in the saturation adsorption capacity with temperature is overlooked, whereas this feature is considered in the nonlinear fitting procedure by incorporating eq 9. Nevertheless, it is not possible from such model fits alone to unequivocally determine the saturation capacities, which are best obtained by actual measurements at very high bulk concentrations approaching the solubility limit. Because of difficulties in accurately determining the amounts adsorbed near saturation using gas chromatographic analysis of the bulk concentrations, this was not attempted here.

The results in Table 2 also show that the fitted expansion coefficients δ for a given component are consistent and essentially independent of the carbon, providing support for the proposed method. The increase of expansion coefficient value with increase of the molecular weight is also observed, as expected. Additionally, the values of δ , of the order of 10^{-3} K^{-1} , are consistent with the value for many liquids,²⁵ although the precise values for the esters used are not readily available. From the results in Table 2 it is also evident that the values of the interaction parameter for a given adsorbate are essentially constant, and substantially independent of the carbon.

4.2. Effect of Bulk Nonideality. The significance of the liquid-phase activities was examined by replacing the relative activity term (a_s/a_c) in eq 24 by the relative concentration (C_s/C_c). The fitting procedure with this

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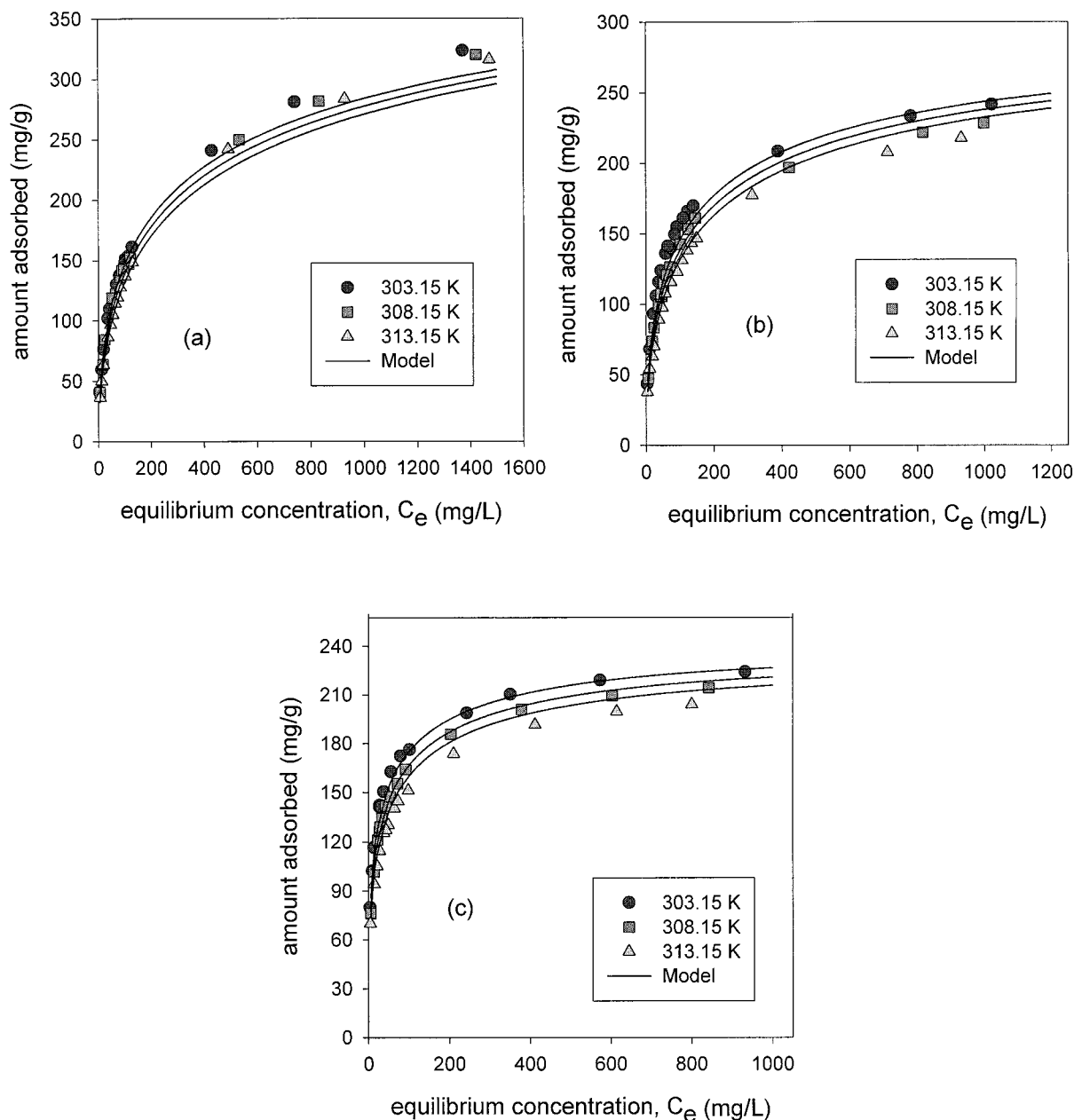


Figure 7. Fit of model isotherm without effect of nonideality for (a) ethyl propionate, (b) ethyl butyrate, and (c) ethyl isovalerate on Norit ROX 0.8 activated carbon.

Table 4. Fitted Parameters of the Model without Effect of Bulk Nonideality, for Norit ROX 0.8 Carbon

parameter	ethyl propionate	ethyl butyrate	ethyl isovalerate
q_{\max} (mg/cm ³)	1073.00	795.38	721.853
σ_{AA} (nm)	0.398	0.499	0.589
τ	0.678	0.451	0.420
$\delta \times 10^3$ (K ⁻¹)	0.203	1.851	3.677
error, $E \times 10^2$ (mg ² /g ²)	5.85	3.49	3.16

method was performed for Norit ROX 0.8 activated carbon, and the estimated values of the model parameters without the effect of nonideality for each ester are given in Table 4. Table 4 clearly shows that the effective molecular sizes σ_{AA} , especially for ethyl propionate and ethyl butyrate, are significantly smaller than those calculated from eq 27. The values of the fitted thermal expansion coefficient δ calculated by this method are also not consistent. Further, the fitting errors are also significantly larger, as is evident from the results presented in Tables 2 and 4. This evidence strongly indicates that the nonideality of

the bulk liquid phase has significant influence and must be included in the isotherm model as proposed.

Figure 7 depicts the isotherm fit for the Norit ROX 0.8 activated carbon using the model without nonideality effect, illustrating the poor agreement between the model and the experimental data. In particular, this model fails to describe the experimental data at high concentration and temperature, and a large deviation between the model and the experimental data, especially for ethyl propionate, is observed. At low-equilibrium concentration (<200 mg/L), the deviation is small, but increases with increase of equilibrium temperature. The deviation between the experimental data and the model for ethyl propionate is larger by as much as 20–25% at the higher concentration, which is clearly due to the greater nonideality of the ethyl propionate-water mixture, as demonstrated in our recent study.¹⁷ In this study we also have shown the significance of liquid-phase activities by investigating the effect of relative concentration on relative activity at the three experimental temperatures for each of adsorptives. For

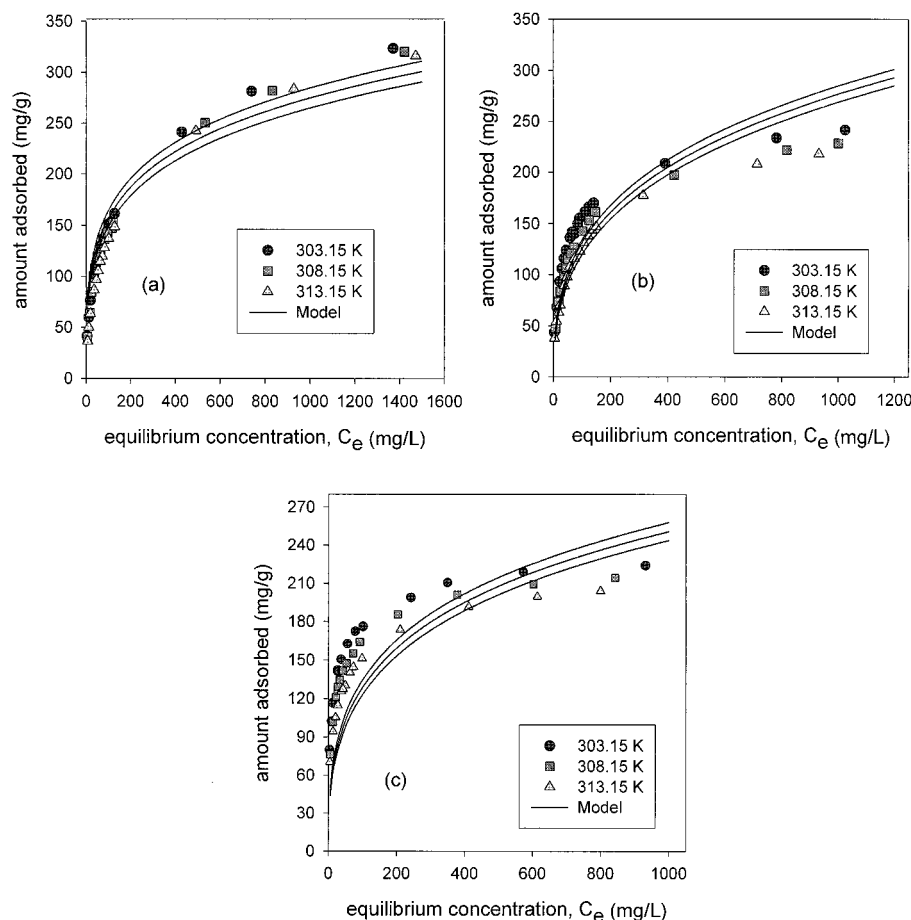


Figure 8. Fit of classical DR model isotherm for (a) ethyl propionate, (b) ethyl butyrate, and (c) ethyl isovalerate on Norit ROX 0.8 activated carbon.

the other esters, a significance difference between these quantities was observed at 313.15 K (at concentration > 200 mg/L). This is consistent with the present results of larger deviations at this temperature, providing further evidence for the importance of incorporating nonideality of the bulk liquid phase in the proposed model.

Although we have accounted for the bulk nonideality in our formulation, the formulation does not consider the isotherm in the form of the surface excess. While that may be essential in significantly more concentrated bulk solutions, in the present case where the solute mole fractions are less than 5×10^{-5} this correction is inconsequential and therefore was not used. Another aspect is that we do not consider adsorption of the water, because it has a relatively much smaller affinity than the esters and an unfavorable type V isotherm. For mixtures of organics, however, the solvent effect may be important and require consideration, as done by Garbacs et al.²⁶ for equal-sized solute and solvent molecules.

4.3. Characteristic Energy Model. As mentioned before the repulsive contribution to the pore potential is important in micropore adsorption, leading to inaccuracy of the usual form of $\beta E_o(H) = \beta k/H$ in the DR equation. For purposes of comparison, in this section we present the isotherm fits using this correlation for the energy in conjunction with eq 23. In this case, for each ester the maximum capacity q_{\max} , thermal expansion coefficient δ , and affinity β were used as the fitting parameters, and Norit ROX 0.8 activated carbon was chosen as the

Table 5. Fitted Parameters for Model Allowing for Bulk Nonideality but Using eq 4 for Characteristic Energy, for Norit ROX 0.8 Carbon

parameter	ethyl propionate	ethyl butyrate	ethyl isovalerate
q_{\max} (mg/cm ³)	1381.64	1103.09	614.38
β	0.529	0.458	0.637
$\delta \times 10^3$ (K ⁻¹)	2.908	3.419	2.495
error, $E \times 10^2$ (mg ² /g ²)	6.91	21.41	19.17

adsorbent. The same calculation procedure used earlier was also applied for this method. Table 5 presents the parameter values obtained from the isotherm fits. Clearly the fitted parameters q_{\max} are significantly larger for ethyl butyrate and smaller for ethyl isovalerate, and yield unreasonable accessible pore volumes compared with those in Table 3.

The solid lines in Figure 8 represents the model fits of the isotherm data on activated carbon Norit ROX 0.8, yielding poor agreement with average deviation more than 25%.

In the usual form of the DR equation, the affinity coefficient β represents an important variable of the pore-filling model. This affinity coefficient is affected by the adsorbate properties such as size and shape, boiling point, and chemistry.²⁷ The value of affinity coefficient can be correlated with physical properties of the molecule such as molecular parachor, molar liquid volumes, and molar polarization,^{28–31} and it is generally assumed that β is proportional to one of these measurable properties. Here

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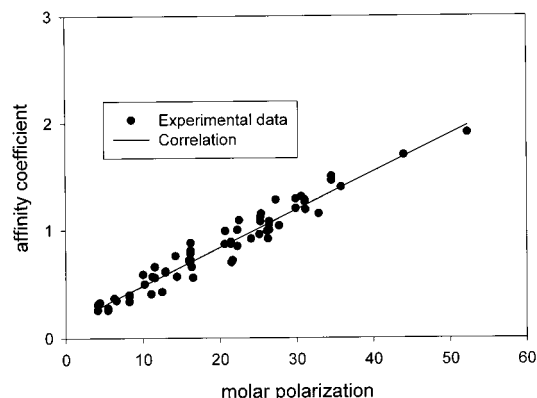


Figure 9. Correlation of affinity coefficient with molar polarization.

we compare the fitted affinity coefficient with its theoretical counterpart calculated from parachors and from molar polarization. Because the parachors for the esters were not available, these were estimated from structural group contribution methods.³⁰ To estimate the values of affinity coefficient from molar polarization we used the data compiled by Wood²⁹ for numerous compounds, which yields a linear correlation as depicted in Figure 9. This correlation is expressed as

$$\beta = 0.1302 + 0.0353P_e \quad (30)$$

with coefficient of correlation 0.971 and standard error of estimated 0.088. Here P_e is molar polarization of the molecules and can be calculated using

$$P_e = \left[\frac{n_D^2 - 1}{n_D^2 + 2} \right] \frac{M}{\rho_L} \quad (31)$$

in which n_D is the refractive index, M is molecular weight, and ρ_L is liquid density. Figure 10 a and b show the correlation between the fitted affinity coefficient values and those estimated from parachor as well as the molar polarization. Clearly the fitted values are approximately 30–40% of the value expected from parachor or molar polarization. In this context, Jaroniec et al.,^{32,33} based on their experiments with liquid- and vapor-phase benzene adsorption, have noted that the values of β for liquid-phase adsorption are about half of those for the gas phase (i.e., the values based on parachor or molar polarization). Although our findings are indeed consistent with this observation, the limitations of the conventional expressions for the characteristic energy are evident. Such limitations have prompted other workers³⁴ to seek alternate ways of improving the predictions of the DR equation for large gas-phase molecules by considering patchwise topography of the solid and interactions among adsorbed molecules, while retaining the characteristic energy form

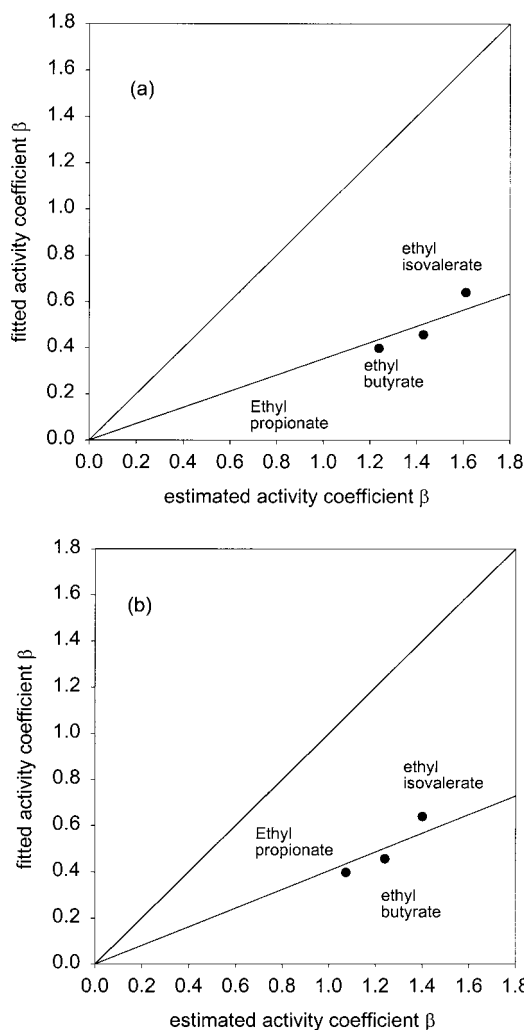


Figure 10. Comparison of fitted and estimated values of affinity coefficient based on (a) parachor and (b) molar polarization.

in eq 4. Similar approaches can also be adopted in conjunction with the modified expression used here to obtain even further refinements, a task that is left open for future study.

5. Summary

A modification of the Dubinin–Radushkevich pore-filling model by incorporation of bulk nonideality and the repulsive contribution to the pore potential is proposed in this article for liquid-phase adsorption. Structural heterogeneity of the carbon also affects the adsorption and is incorporated based on pore-size distribution obtained by DFT analysis of argon adsorption. The modified model was tested using liquid-phase adsorption isotherm data of three flavor esters over three different commercial activated carbons, and yielded excellent agreement with the experimental data. In particular, the comparison with the results of application of the classical DR model have demonstrated the importance of considering bulk nonideality and the repulsive contribution to the pore potential. The latter is incorporated through a Lennard–Jones interaction potential model, and the fitted values of the adsorbate size parameter and other parameters are consistent with those expected.

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