CHARACTERIZATION OF ACTIVATED CARBONS USING LIQUID PHASE ADSORPTION

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Introduction

The pore size distribution is the most important aspect in characterization of structural heterogeneity of porous materials. Different methods have been developed and applied for the characterization of this property, and the most often used is gas adsorption [1,2], while liquid phase adsorption is seldom used [3]. A modification of the Dubinin-Radushkevich pore filling by incorporation of the repulsive contribution to the pore potential, and bulk nonideality, is proposed in this paper for characterization of three commercial activated carbons (Filtrasorb-400, Norit ROW 0.8, and Norit ROX 0.8) using liquid phase adsorption of flavor esters (ethyl propionate, ethyl butyrate, and ethyl isovalerate). The bulk-liquid phase nonideality is incorporated through the UNIFAC activity coefficient model, and the repulsive contribution to the pore potential incorporated through the Steele 10-4-3 potential model. The bimodal gamma function was utilized as the pore size distribution in the generalized adsorption isotherm. Excellent agreement between the bimodal gamma pore size distribution and DFT-cum-regularization based pore size distribution is also observed, supporting the validity of the proposed model.

Experimental

Food grade and commercially available coal based activated carbons Filtrasorb-400, Norit ROW 0.8 and Norit ROX 0.8 were used as the adsorbents in this study. Structural characteristics of activated carbons are summarized in Table 1. Analytical grade ethyl propionate, ethyl butyrate, and ethyl isovalerate with purity about 98-99 % were used as the adsorbates.

The liquid phase adsorption experiments were carried out isothermally in static mode at three different temperatures, 303.15 K, 308.15 K, and 313.15 K. A fixed amount of activated carbons were added to a series of 250 mL glass-stoppered flask filled with 200 mL of dilute solutions. These were then placed in a thermostatic shaker bath and shaken at 120 rpm for at least two days. Details of the adsorption experiments can be found elsewhere [4]. The initial and equilibrium concentration of all solutions were determined by means of Shimadzu gas chromatograph (GC-17A) provided with a flame ionization detector (FID)

Mathematical Model

The equation used for interpretation of adsorption equilibrium data to characterized the structural heterogeneity of activated carbons is as follows

$$N(T,C) = \int_{d_c}^{\infty} n_\infty \exp\left[-\left(\frac{RT \ln(a_e/a_s)}{\tau\left[\Lambda(H',z_{min}) - \Lambda^\infty(z_{min}^\infty)\right]}\right)^2\right] f(H) dH \quad (1)$$

Here $N(T,C)$ is amount adsorbed per unit mass of adsorbent at temperature T and adsorptive concentration C, and d_c is critical molecular size of the compound. The terms of a_e and a_s are the activities of the adsorptive in the bulk liquid at equilibrium and at saturation respectively, and H is the slit pore width. The term of a_e/a_s in eq. 1 represents the non-ideality of bulk liquid phase, which replaces the term of C_e/C_s in the original DR equation. The adsorption energy in pores is represented by the term $\tau\left[\Lambda(H',z_{min}) - \Lambda^\infty(z_{min}^\infty)\right]$, which is a modification of the DR characteristic energy. Here τ is a fitted interaction parameter, and H' is center to center distance between carbon atoms on opposing pore walls, and equal to $H + 0.3354$. The location at which the minimum values of the adsorption potential in the micropore and on the flat surface achieved are z_{min} and z_{min}^∞, respectively. The total pore potential in the micropore, $\Lambda(H',z_{min})$, can be expressed as

$$\Lambda(H',z_{min}) = \Phi_{CA}(z_{min}) + \Phi_{CA}(H'-z_{min}) \quad (2)$$

and that on the flat surface, $\Lambda^\infty(z_{min}^\infty)$, is taken as

$$\Lambda^\infty(z_{min}^\infty) = \Phi_{CA}(z_{min}^\infty) \quad (3)$$

here Φ_{CA} was determined by the Steele 10-4-3 potential model.

The temperature dependence form of the maximum capacity, n_∞, can be written in the following form

$$n_\infty = n_\infty^o \exp\left[\delta(T_o - T)\right] \quad (4)$$

where n_∞^o is the maximum capacity at reference temperature T_o (taken here as 303.15 K), and δ is coefficient of expansion of the adsorbate. The pore size distribution $f(H)$ has the following bimodal form

$$f(H) = b_1 \frac{q_1^{\gamma_1+1} H^{\gamma_1} e^{-q_1 H}}{\Gamma(\gamma_1+1)} + b_2 \frac{q_2^{\gamma_2+1} H^{\gamma_2} e^{-q_2 H}}{\Gamma(\gamma_2+1)} \quad (5)$$

where $\Gamma(\gamma_i+1)$ is the gamma function, and q_i and γ_i are pore structural parameters.

Results and Discussion

Figure 1 depicts the experimental adsorption isotherm data and model representation of ethyl propionate, ehtyl butyrate and ethyl isovalerate on Filtrasorb 400. Clearly, the experimental data are well described by our proposed model. Similar results were also observed for the other compounds in others different carbons, details of which can be seen in elsewhere [5].

Figure 2 compares the normalized pore size distribution for each of the carbons as obtained from our proposed model, with that obtained based on argon adsorption using DFT with regularization. From this figure it can be observed that the modal pore widths of the carbons obtained from fitting are only marginally higher than that from DFT analysis using argon adsorption. The small difference of the pore size distribution obtained from DFT based distribution and our current model is most likely due to the constraint of gamma function form, which cannot precisely describe certain parts of the pore size distribution. It is apparent that the bimodal gamma distribution can also describe the pore size distribution very well.

Conclusions

A modification of the DR approach for characterization of activated carbon using liquid phase adsorption is proposed in this paper. The new approach yields consistent parameters, and the pore size distributions obtained based on a bimodal gamma function are similar to those obtained from DFT using argon analysis, supporting our proposed model.

References

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3. Choma J, Burakiewicz-Mirtka W, Jaroniec M and Gilpin RK. Studies of the Structural Heterogeneity of Microporous Carbons Using Liquid/Solid Adsorption Isotherms. Langmuir 1993; 9: 2555-2561.
4. Ismadji S and Bhatia SK. Investigation of Network Connectivity in Activated Carbons by Liquid Phase Adsorption. Langmuir 2000; 16 (24): 9303-9313.
5. Ismadji S and Bhatia SK. Characterization of Activated Carbons Using Liquid Phase Adsorption. Carbon 2001; In press.

Table 1. Structural characteristic of activated carbons

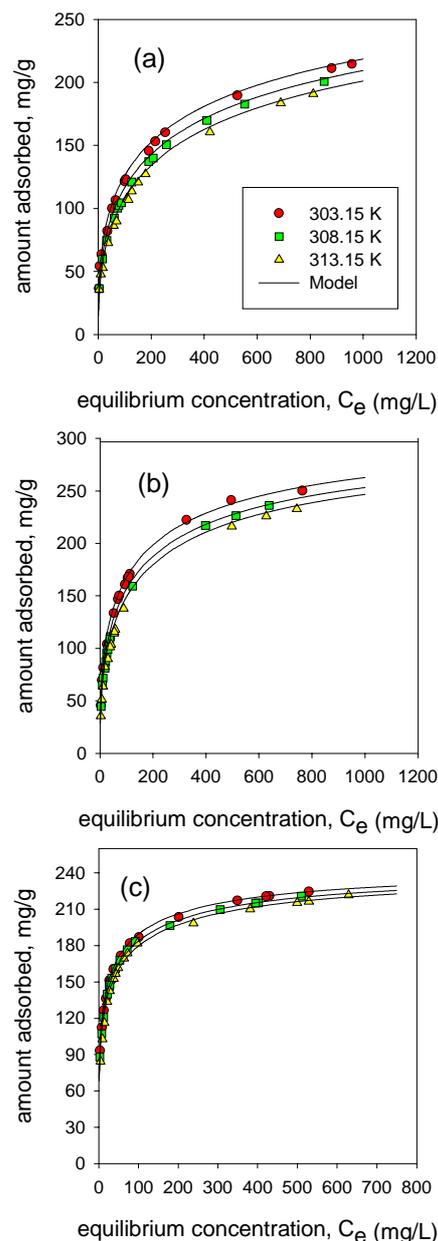| Sorption characteristic	F-400	Norit ROW 0.8	Norit ROX 0.8
BET surface area (m^2/g)	877.82	849.39	978.85
Micropore surface area (m^2/g)	761.80	718.00	847.00
Micropore volume (cm^3/g)	0.343	0.314	0.365
Total pore volume (cm^3/g)	0.468	0.443	0.467

Figure 1. Experimental adsorption isotherms and fit of model for flavor esters on Filtrasorb 400. (a) ethyl propionate, (b) ethyl butyrate, and (c) ethyl isovalerate
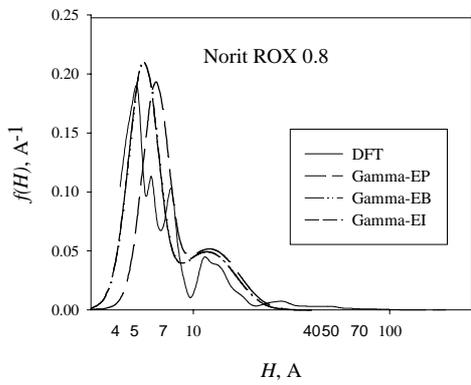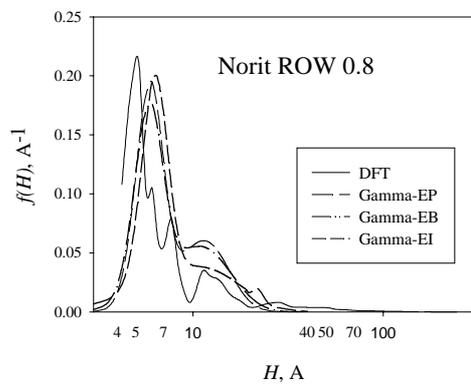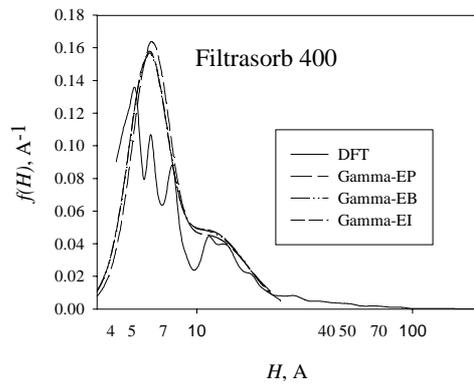
Figure 2. Pore size distribution of activated carbons