Adsorption equilibria of VOCs (*n*-octane, propylene glycol monomethyl ether, ethanol, and 2-propanol) on activated carbon under supercritical carbon dioxide conditions

Ikuo Ushiki [a], *, Koichi Kikuchi [b], Yoshiyuki Sato [b], Yasuyuki Ito [c], Shigeki Takishima [a], Hiroshi Inomata [b], **

[a] *Department of Chemical Engineering, Graduate School of Engineering, Hiroshima University, Kagamiyama, 1-4-1-335, Higashi-Hiroshima, Hiroshima 739-8527, Japan*
[b] *Research Center of Supercritical Fluid Technology, Graduate School of Engineering, Tohoku University, Aramaki Aza Aoba, 6-6-11-404, Aoba-Ku, Sendai, Miyagi 980-8579, Japan*
[c] *Technical Research Laboratory, DAI-DAN Co., Ltd., Kitanagai, 390, Miyoshimachi, Irumagun, Saitama 354-0044 Japan*

ARTICLE INFO

ABSTRACT

Adsorption equilibria of volatile organic compounds (VOCs: *n*-octane, propylene glycol monomethyl ether, ethanol, and 2-propanol) on activated carbon were measured using the fixed-bed method under supercritical carbon dioxide (scCO$_2$) conditions at 313—353 K and 10.0—15.0 MPa. The measured adsorption isotherms strongly depended on the properties of the VOCs together with the CO$_2$ density. The adsorption equilibria were correlated using the Dubinin–Astakhov (DA) equation with two fitting parameters: E_{VOC} (the interaction energy between VOC and adsorbent) and $W_{0,VOC}$ (the saturated adsorption capacity of VOC). The fitting parameters provided insight into the adsorption phenomena of VOCs in scCO$_2$ in terms of the CO$_2$ density and properties of VOCs.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Activated carbon is one of the most promising adsorbents for removing hazardous substances such as volatile organic compounds (VOCs) [1,2]. Regeneration of activated carbon allows its reuse in industrial processes, with economic and environmental benefits [3]. Thermal regeneration methods have traditionally been used in many industries. However, these methods can damage the pore structure of activated carbon and cause carbonization of adsorbates, owing to the high operating temperatures (over 1000 K) that are generally required [4,5].

Supercritical carbon dioxide (scCO$_2$) is an effective solvent for the regeneration of activated carbon. Regeneration in scCO$_2$ can be carried out at relatively low temperatures (critical temperature (T_c),

304.12 K [6]), and the solvent has extremely low surface tension, resulting in less damage to the structure of the adsorbent and high levels of diffusion into its micropores. The desorption behaviors of various VOCs under scCO$_2$ conditions have previously been studied with a view to optimizing the design of the regeneration process [7—17].

The efficient design of such desorption and regeneration processes also requires adsorption equilibrium data in scCO$_2$. Some researchers have investigated the adsorption equilibria of various VOCs in scCO$_2$ [13,14,18—22]. However, most studies have focused on only one or two VOCs; therefore, little attention has been paid to how the properties of VOCs affect adsorption equilibria on activated carbon in scCO$_2$. We have earlier [23,24] reported the adsorption equilibria of various VOCs (acetone, *n*-hexane, toluene, *n*-decane, and methanol) on activated carbon under scCO$_2$ conditions, and investigated the effects of such VOCs on the adsorption equilibria. We showed that the adsorption equilibria strongly depended on the properties of VOCs, in particular, the affinity of the VOCs for the adsorbent. Adsorption equilibrium data for other VOCs are necessary for a more detailed understanding of the effects of the

---

* Corresponding author.
** Corresponding author.
 E-mail addresses: iushiki@hiroshima-u.ac.jp (I. Ushiki), inomata@scf.che.tohoku.ac.jp (H. Inomata).

properties of VOCs on adsorption phenomena.

In this study, four VOCs with different properties, n-octane, propylene glycol monomethyl ether (PGME), ethanol, and 2-propanol, were selected as target VOCs, and adsorption equilibria of these VOCs on activated carbon under scCO$_2$ conditions (temperature 313—353 K, pressure 10.0—15.0 MPa) were investigated. Here, we first compare the adsorption equilibria of the VOCs on activated carbon measured in this study with previously reported adsorption equilibrium data [23,24]. Next, correlations of the measured data are presented using the Dubinin—Astakhov (DA) equation [25], which has fitting parameters with clear physical meanings and high applicability to the scCO$_2$ systems [24,26], in comparison with conventional models such as the Langmuir [27] and Freundlich [28] equations. Finally, the determined fitting parameters are discussed for a quantitative description of the adsorption phenomena of the various VOCs in scCO$_2$ systems.

2. Experimental

2.1. Materials

Ethanol (purity: 99.5 mass%), 2-propanol (purity: 99.7 mass%), and n-octane (purity: 98.0 mass%) were obtained from Wako Pure Chemical Industries, Japan. PGME (purity: 99.5 mass%) was purchased from Sigma-Aldrich Co. LLC., USA. Carbon dioxide (purity: 99.99 vol%) was obtained from Showa Denko Gas Products Co. Ltd., Japan. These chemicals were used without further purification. The purity and supplier of the chemicals are summarized in Table 1. Activated carbon was supplied from Cambridge Filter Japan, Ltd. Specific surface area (1300 m^2/g), mean pore diameter (0.69 nm), and pore volume (0.441 cm^3/g) of the adsorbent were determined by the t method [29] using a nitrogen adsorption measurement apparatus (Belsorp mini, MicrotracBEL Co., Japan). Pore size distribution of the adsorbent determined with the nitrogen adsorption measurement is shown in Fig. S1. The adsorbent was loaded into an adsorption column (1/4-inch SUS316 tube, length: 100 mm, inner diameter: 4.35 mm, mass of adsorbent: 0.71 g, void fraction: 0.55), and pretreated by heating in an argon gas atmosphere at 573 K for 12 h to remove possible impurities and water.

2.2. Measurement of adsorption equilibria

Adsorption equilibria of the VOCs on activated carbon under scCO$_2$ conditions were measured using the fixed-bed method [24] at temperatures from 313 to 353 K and pressures from 10.0 to 15.0 MPa. Details of the experimental apparatus and procedure have been described in a previous work [24].

3. Model

The Dubinin—Astakhov (DA) equation [25] is a semi-empirical thermodynamic model based on the potential theory proposed by Polanyi [30]. The DA equation was originally developed for investigating the adsorption of pure gases [25], and was later extended to the adsorption of VOCs in scCO$_2$ as follows [24,26]:

$$W_{\mathrm{VOC}} = W_{0,\mathrm{VOC}} \exp\left[-\left(\frac{\varepsilon_{\mathrm{VOC}}}{E_{\mathrm{VOC}}}\right)^n \right] \tag{1}$$

$$\varepsilon_{\mathrm{VOC}} = RT \ln\left[\frac{f^s_{\mathrm{VOC}}(T)}{f_{\mathrm{VOC}}(T,P,y_{\mathrm{VOC}})}\right] \tag{2}$$

$$q_{\mathrm{VOC}} = \frac{\rho W_{\mathrm{VOC}}}{M} \tag{3}$$

where W_{VOC} and q_{VOC} are the amount of the adsorbed VOC, on a volume and a molar basis, respectively. E_{VOC} is the interaction energy between VOC and the adsorbent, and $W_{0,\mathrm{VOC}}$ is the saturated adsorption capacity of VOC in scCO$_2$. In Eq. (2), $\varepsilon_{\mathrm{VOC}}$ is the adsorption potential of VOC on the adsorbents in scCO$_2$; f_{VOC} is the fugacity of VOC in the bulk phase at a given temperature (T), pressure (P), and molar fraction of VOC (y_{VOC}), and f^s_{VOC} is the saturated fugacity of VOC at T. These fugacities were calculated using the Peng—Robinson equation of state [31]. In the calculation of f_{VOC}, the binary interaction parameter (k_{ij}) in the van der Waals one-fluid mixing rule [32] were determined by fitting to vapor − liquid equilibrium data of corresponding CO$_2$-VOC binary systems at 313—353 K ($k_{ij} = 0.101$, 0.096, and 0.118 for n-octane [33], ethanol [34], and 2-propanol [35], respectively) except for PGME. Since vapor-liquid equilibrium data for CO$_2$ − PGME system were not available, k_{ij} for PGME was assumed to be equal to 0.1. The critical properties and acentric factors of the components were obtained from the literature [6,36]. In Eq. (1), n is a dimensionless parameter that was fixed at a value of 2 based on the recommendation of Suzuki for its use with activated carbon [37]. In Eq. (3), M is the molar mass of the VOC and ρ is the density of the VOC in the adsorbed phase; ρ was assumed to be its saturated liquid density [38] at the operating temperature.

The measured adsorption equilibria of VOCs on activated carbon in scCO$_2$ were correlated with the two fitting parameters in Eq. (1), E_{VOC} and $W_{0,\mathrm{VOC}}$. The objective function used in the correlation was the average relative deviation (ARD), defined as follows.

$$\mathrm{ARD}[\%] = \frac{1}{N}\sum_i \left|\frac{q_{\mathrm{corr},i} - q_{\mathrm{exp},i}}{q_{\mathrm{exp},i}}\right| \times 100 \tag{4}$$

where q_{corr} and q_{exp} are correlated and experimental values of the amount of adsorbed VOC, respectively.

4. Results and discussion

4.1. Experimental results

4.1.1. Pressure dependence of adsorption equilibria in scCO$_2$

Fig. 1 shows adsorption equilibria of VOCs (n-octane, PGME, ethanol, and 2-propanol) on activated carbon in scCO$_2$ at pressures from 10.0 to 15.0 MPa and at temperatures from 313 to 353 K. The experimental values of the amount of adsorbed VOC are summarized in Tables S1—S4 (supplementary material). These results

Table 1
Purity and supplier of chemicals.

	n-Octane	PGME[b]	Ethanol	2-Propanol	Carbon dioxide
Purity (mass%)	98.0	99.5	99.5	99.7	99.99[a]
Supplier	Wako Pure Chemical	Sigma- Aldrich	Wako Pure Chemical	Wako Pure Chemical	Showa Denko Gas Products
Purification method	None	None	None	None	None

[a] Vol%.
[b] Propylene glycol monomethyl ether (IUPAC name: 1-Methoxy-2-propanol).