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Measurements of binary diffusion coefficients and retention factors for dibenzo-24-crown-8 and 15-crown-5 in supercritical carbon dioxide by chromatographic impulse response technique

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Abstract

Binary diffusion coefficients D_{12} and retention factors k for dibenzo-24-crown-8 and 15-crown-5 ethers at 308.18 and 313.20 K, and vitamin K_1 at 313.20 K were measured in supercritical carbon dioxide by the chromatographic impulse response technique, and the effects of molecular shapes on the D_{12} values were studied. At 313.2 K and 11.0 MPa the D_{12} value of 15-crown-5 was higher than that predicted from the D_{12} correlation with molecular weight MW over the range from 32 of methanol to 1138 of trinervonin reported in our previous studies, while the D_{12} value of dibenzo-24-crown-8, disk shape molecule with MW = 448.5, was almost in agreement with that of vitamin K_1, long chain molecule with MW = 450.7, and with those predicted from the correlation.

Keywords: Binary diffusion coefficient; Chromatographic impulse response; 15-Crown-5; Dibenzo-24-crown-8; Retention factor; Supercritical carbon dioxide; Vitamin K_1

1. Introduction

Supercritical fluids have been employed as not only solvents in extraction and fractionation but also reaction media in synthetic, polymerizing and decomposition reactions. Binary diffusion coefficient D_{12} is one of the important physical properties for designing reactors, and a large number of D_{12} measurements for various compounds in supercritical fluids have been made [1,2]. Recently, we found that D_{12} values were primarily affected by solute molecular weight, and secondarily by the solute polarity [3]. Moreover, the D_{12} values at 313.2 K and 11.0 MPa were expressed with a straight line in logarithmic plots of D_{12} value versus molecular weight MW with a slope of −0.5 [2]. However, most measured compounds having large molecular weights are long chain molecules, and the effect of the molecular shape on D_{12} value is not well understood. Although binary diffusion coefficients of disk shape molecules such as various crown ethers were measured in organic solvents at an ambient pressure [4–8], those in supercritical fluids are not available in the literature. Thus, the objectives in this study are to measure D_{12} values for disk shape molecules, i.e. dibenzo-24-crown-8 and 15-crown-5, and to investigate the effect of molecular shapes on D_{12} values in supercritical carbon dioxide, as compared with vitamin K_1 having a long chain shape and the nearly same molecular weight as dibenzo-24-crown-8.

2. Theory

The theory for the chromatographic impulse response technique was described in detail in elsewhere [9,10]. When a tracer is pulse-injected into a fully developed laminar flow in a coated cylindrical column, the cross-sectional average concentration $C_a(t)$ can be described as follows:

$$C_a(t) = \left(\frac{m}{\pi R^2}\right) \frac{1}{(1+k)\sqrt{4\pi a t}} \exp\left\{-\frac{(L - u_a t/(1+k))^2}{4at}\right\} \quad (1)$$

$$a = \frac{D_{12}}{1+k} + \frac{1+6k+11k^2}{(1+k)^3} \frac{R^2 u_a^2}{48 D_{12}} \quad (2)$$

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where m is the amount of the tracer species, R the radius, t the time, L the distance, u_a the average fluid velocity, k the retention factor, and D_{12} the binary diffusion coefficient of the tracer species. When u_a is measured, D_{12} and k can be simultaneously determined by minimizing the root-mean-square (rms) error ε, defined by Eq. (3), for the measured $C_{exp}(t)$ and calculated $C_a(t)$ curves.

$$\varepsilon = \left\{ \frac{\int_{t_1}^{t_2} (C_a(t) - C_{exp}(t))^2 \, dt}{\int_{t_1}^{t_2} (C_{exp}(t))^2 \, dt} \right\}^{1/2} \quad (3)$$

where t_1 and t_2 are chosen as the times at the front and latter 10% peak heights, respectively, of the measured response curve to exclude possible tailing portions of the response curves.

3. Experimental

3.1. Chemicals

Dibenzo-24-crown-8 (2,3,14,15-dibenzo-1,4,7,10,13,16,19,22-octaoxacyclotetracosa-2,14-diene, purity of 98%), 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane, 98%), and acetone (99.5%) were purchased from Aldrich (USA), and vitamin K_1 (2-methyl-3-phytyl-1,4-naphthoquinone, no information on purity) and hexane (99%) from Sigma (USA). These reagents were used without further purification. Note that no other peaks appeared in the two dimensional chromatogram of wavelength against time when vitamin K_1 was loaded to the diffusion column. CO_2 (99.995%, contains water <40 ppm) was obtained from Showa Tansan Co., Japan.

3.2. Equipment and procedure

The experimental apparatus and procedures are substantially the same as those in the previous studies [9,11], and briefly described below. A diffusion column used was a poly(ethylene glycol) coated capillary column (UACW-15W-1.0F, the Frontier Laboratories Ltd., Japan) with polymer thickness of 1 μm, 0.515 mm I.D., 15.10 m long, and coil diameter of 0.27 m. CO_2 was fed by a syringe pump (100DX, ISCO, USA), and measurement was started after further passing 2–3 h from the moment that the flow system had become stabilized. A solute dissolved in an organic solvent (a 0.5 μL acetone solution of dibenzo-24-crown-8 at a concentration of 3–8 kg m^{-3}, a 0.2 μL hexane solution of 15-crown-5 at 5 kg m^{-3}, and a 0.5 μL supercritical CO_2 solution of vitamin K_1) through an HPLC injector (Model 7520, Rheodyne, USA) into the diffusion column. In the course of each measurement CO_2 flow rates were measured with a soap-bubble flow meter several times. Response curves, as time changes of the tracer concentration, in terms of absorbance spectra were monitored with a high-pressure multi-UV detector (MD-1510, JASCO, Japan) by scanning at wavelengths from 195 to 400 nm with increments of 1 nm and time interval of 1.6 s. By examining the wavelength dependences on the response curve intensity, the values of D_{12}, k and ε, as described for various solutes in our previous studies [1,2,9–11], the response curves monitored at 275, 200 and 325 nm were used to determine the D_{12} and k values for dibenzo-24-crown-8, 15-crown-5, and vitamin K_1, respectively. Note that the solubility of dibenzo-24-crown-8 in supercritical carbon dioxide [12] is much lower than that of 15-crown-5.

All measurements were made at $DeSc^{1/2} < 8$, which is a criterion for the secondary flow effect due to a diffusion column coiling, and corresponds to less than 1% of the effect on D_{12} value in terms of the second moment [13], where De and Sc are the Dean number and Schmidt number, respectively. The CO_2 densities were obtained with the equations of Pitzer and Schreiber [14] and Span and Wagner [15], and the viscosities were estimated by the method of Fenghour et al. [16].

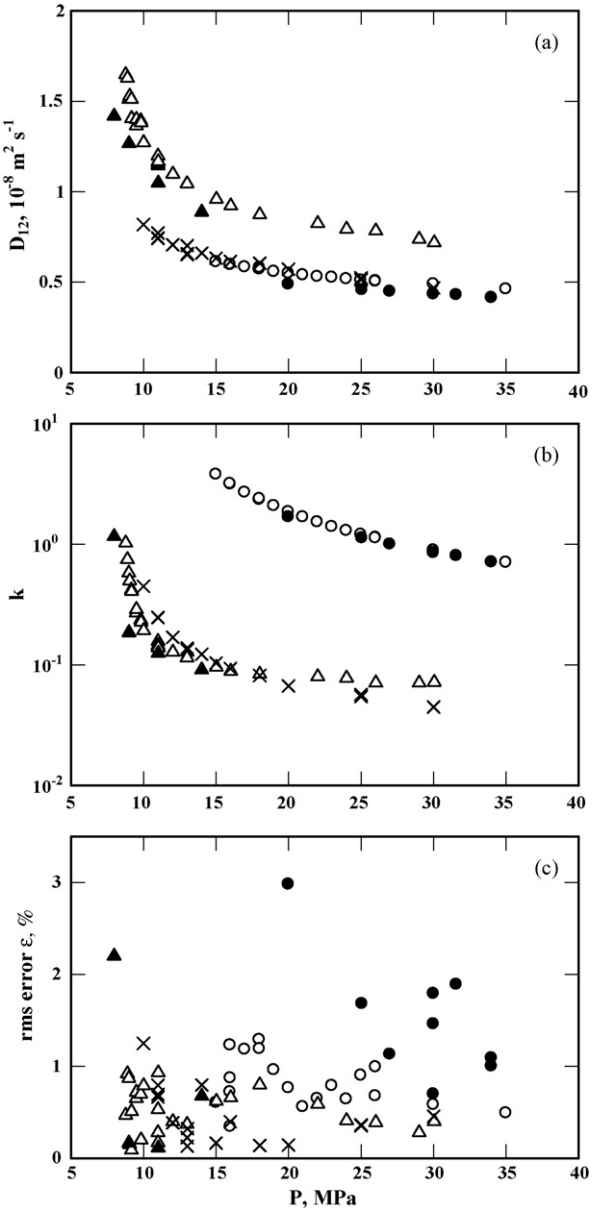

Fig. 1. Pressure dependences on (a) D_{12}, (b) k, and (c) ε for dibenzo-24-crown-8 (circle) and 15-crown-5 (triangle) at 308.18 K (solid key) and 313.20 K (blank key), and vitamin K_1 (cross) at 313.20 K.