Distribution Behavior of 2-Methyl-5-hexyloxymethyl-8-quinolinol between Supercritical CO_2 and Water

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The distribution constants ($K_{D,\mathrm{SF\ CO2}}$) of 2-methyl-5-hexyloxymethyl-8-quinolinol (HMO_6Q) between supercritical (SF) CO_2 and water were determined at I = 0,1 M (H,Na)NO_3 (1 M = 1 mol dm^{-3}), 45 °C and 8.6 - 20.4 MPa. The log $K_{D,\mathrm{\ SF\ CO2}}$ values at 8.6, 12.2, 15.7, and 20.4 MPa were 1.18 ± 0.13, 1.76 ± 0.14, 2.18 ± 0.17, and 3.02 ± 0.21, respectively. The $K_{D,\mathrm{SF\ CO2}}$ value at 20.4 MPa was about one tenth of that (log K_D = 4.08 ± 0.02) for the heptane-water system at 45 °C and an atmosphere.

A solvent-extraction teqnique has been widely used for the pre-concentration and separation of metal ions with extractants in the fields of analytical chemistry, radiochemistry, and hydrometallurgy. More recently, a SF CO_2 extraction method as a separation technique of metal ions has been an attractive and potential technique because of easy removal of CO_2 from extracts.[1-5] In addition, CO_2 is characterized by non toxicity and moderate critical constants (T_c = 32 °C, P_c = 7.3 MPa). We previously reported that gallium(III) was selectively separated from aluminum(III) with HMO_6Q into SF CO_2.[6]

Until now there have been few reports on the SF extraction equilibrium ofmetal chelates.[7] Accordingly, to develop a systematic SF CO_2 separation system for metal ions with chelating extractants, basic data, such as distribution constants of extractants between SF CO_2 and water, are essential to determine the SF extraction constants.

In order to determine the distribution constant of acidic chelating extractants between SF CO_2 and water, the pH value of an aqueous phase contacting with SF CO_2 should be precisely determined. Indeed, it is fairly difficult to directly measure the pH of an aqueous solution equilibrated with SF CO_2 in a high-pressure extraction cell.

In this study, the pH of an acidic solution contacting with SF CO_2 was indirectly and precisely measured by spectrometry according to Wai's method.[8] Furthermore, the distribution constants of HMO_6Q between SF CO_2 and water were determined at I = 0.1 M (H, Na)NO_3, 45 °C, and 8.6 - 20.4 MPa.

HMO_6Q was prepared by our previous method.[9] All other chemicals were of analytical reagent grade.

SF CO_2 extractions were carried out by an apparatus composed of syringe pump (Isco, Model 500D), a pump controller (IASC, Series D), back-pressure regulator (JASCO 880-81), a 50-ml high-pressure stainless-steel extraction cell, and a UV/VIS absorption spectrophotometer (JASCO MD-910) with a high-pressured cell (0.2 ml, 1 cm in length) (Figure 1). The spectrophotometric cell was thermostated by circulating water from a thermostated water bath. The extraction cell was thermostated by a muntle heater with a temperature controller (Omron R5BX). The temperature of the extraction cell and the spectrophotometric cell were monitored with a digital temperature indicator (Fenwal). The pressure of the extraction cell was monitored with a digital pressure indicator (Toyo Sokki). The pH of an aqueous phase in contact with an atmosphere was measured using a pH meter with a glass electrode thermostated at 45 °C.

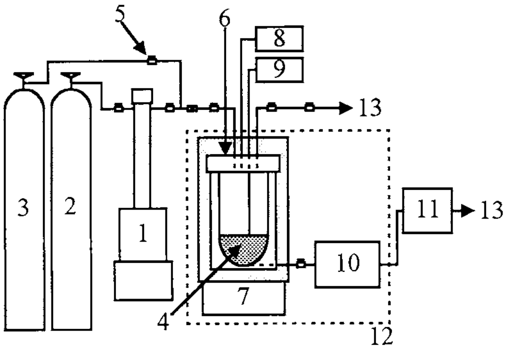


Figure 1. Apparatus for the extraction with supercritical CO_2.
1, Syringe pump and controller; 2, liquid CO_2 cylinder; 3, N_2 cylinder; 4, sample; 5, stop valve; 6, extraction cell; 7, magnetic stirrer; 8, pressure probe; 9, tem.indicator; 10, UV-vis spectrophotometer; 11, back pressure regulator; 12, oven; 13, CO_2 and N_2.

Bromophenol blue (BPB) gives the absorption maxima at 435 and 591 nm in a weakly acidic solution. Wai et al. have proved that plots of $A_{435\mathrm{nm}}/A_{591\mathrm{nm}}$ *vs.* [H^+] gave a straight line under the given conditions, where $A_{435\mathrm{nm}}$ and $A_{591\mathrm{nm}}$ are the absorbances at 435 nm and 591 nm, respectively. It was also found that the plots of $A_{435\mathrm{nm}}/A_{591\mathrm{nm}}$ *vs.* [H^+] for thymol blue gave a straight line. The pH of an aqueous solution in contact with SF CO_2 can be determined by comparing with a calibration curve prepared without contacting with SF CO_2. Before preparing the calibration curve, the stability of BPB in an aqueous solution contacting with SF CO_2 for 45 min at 45 °C and 8.6 MPa was tested. BPB decomposed very slightly. Consequently, the contact time of SF CO_2 was maintained for 15 min. By contacting SF CO_2 with an aqueous solution, the absorbance at 435 nm increased and that at 591 nm decreased. The spectral change should be ascribed to a change in the pH of the aqueous solution due to the dissolution of CO_2.

The relationship between the hydrogen ion concentration of the aqueous phase before contact with SF CO_2 and that in contact with SF CO_2 is shown in Figure 2. Below pH 3, the pH change is negligibly small. On the other hand, above pH 3, the pH of the aqueous phase in equilibrium with SF CO_2 was levelled to about 3. The pH value of the aqueous phase equilibrated with SF CO_2 can be evaluated within an experimental error of 0.1 using Figure 2.

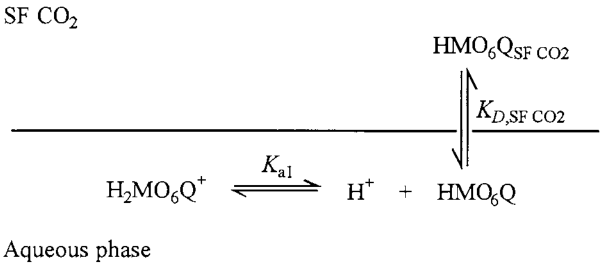
The procedure for the determination of the distribution of HMO_6Q between SF CO_2 and water was as follows, 10 ml of an aqueous acidic solution of 1.00 x 10^{-5} M HMO_6Q was taken in the extraction cell. A syringe pump was filled with CO_2

(99.99% purity) from a liquid CO_2 cylinder and then pressurized by the pump controller. Pressurized liquid CO_2 was introduced into the pre-heated extraction cell. The extraction was carried out under the stirring of the aqueous solution containing HMO_6Q. After 15 min, the outlet valve was opened while regulating the cell pressure by back-pressure regullator and the absorption spectrum of the aqueous phase was measured. Since the ratio of the aqueous phase to the SF CO_2 volume is 1 : 4, the distribution ratio (D) was calculated by using

$$D = (A_o - A_{eq}) / 4 A_{eq}, \qquad (1)$$

where, A_o and A_{eq} are the absorbances at 275.5 nm in the aqueous phase before and after the distribution, respectively.

The absorption maxima of HMO_6Q in SF CO_2 appeared at 310 and 240 nm and the absorption spectra are very similar to those in heptane. The extraction equilibrium of HMO_6Q between SF CO_2 and an acidic aqueous phase can be represented as follows:



where K_{a1} is the acid-dissociation constant of $H_2MO_6Q^+$ in an aqueous phase. Equation (2) was used to determine K_{a1} and $K_{D,SF\ CO2}$. If plots of log $D_{SF\ CO2}$ *vs.* pH are possible in the pH

$$D_{SF\ CO2} = K_{D,SF\ CO2} / ([H^+] K_{a1}^{-1} + 1), \qquad (2)$$

range of 1 - 8, both K_{a1} and $K_{D,SF\ CO2}$ can be simultaneously determined. However, as mentioned above, the acidity of a weakly acidic solution (pH > 3) contacted with SF CO_2 is levelled to about pH 3 by CO_2 dissolved in the aqueous phase Therefore K_{a1} and $K_{D,SF\ CO2}$ cannot be simultaneously determined by plots of log $D_{SF\ CO2}$ *vs.* pH.

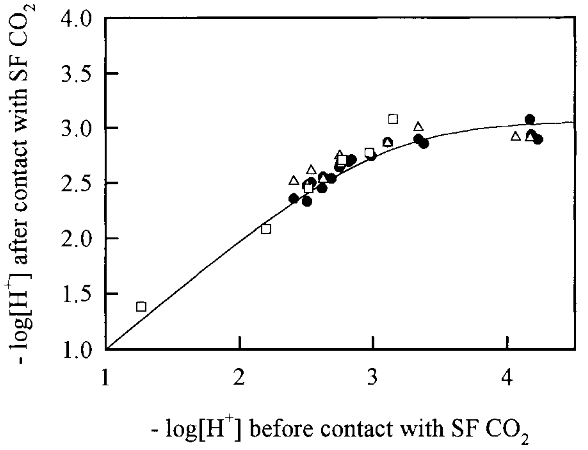


Figure 2. Relationship between - log[H^+] before contact with SF CO_2 and - log[H^+] after contact with SF CO_2.
● : Bromophenol blue, 2.27 × 10^{-5} M; CO_2, 8.6 MPa,
△ : Bromophenol blue, 2.27 × 10^{-5} M; CO_2, 15.7 MPa,
□ : Thymol blue, 5.12 × 10^{-5} M; CO_2, 8.6 MPa.

Table 1. Distribution constants of HMO_6Q at 45℃

Solvent	log K_D
SF CO_2	1.18±0.13[a]
	1.76±0.14[b]
	2.18±0.17[c]
	3.02±0.21[d]
Heptane	4.08±0.02

I = 0.1 M (H, Na)NO_3.
[a]8.6 MPa; [b]12.2 MPa; [c]15.7 MPa; [d]20.4 MPa.

If K_{a1} is known, $K_{D,SF\ CO2}$ can be determined by applying a nonlinear least-squares method based on Equation (2) to plots of log $D_{SF\ CO2}$ *vs.* pH. The slope of the straight line of the plots of log $D_{SF\ CO2}$ *vs.* pH should be one. The log $D_{SF\ CO2}$ value at a pH value equal to pK_{a1} corresponds to the logarithmic value of $K_{D,SF\ CO2}$, where the pH values of the aqueous phase equilibrated with SF CO_2 were determined from the data shown in Figure 2. The K_{a1} value of HMO_6Q was independenly determined by plotting log D *vs.* pH for a heptane - water system. The pK_{a1} value for HMO_6Q was 4.89 at I = 0.1 M (H, Na)NO_3 and 45 °C. The plots of log $D_{SF\ CO2}$ *vs.* pH for HMO_6Q-SF CO_2 - water system gave a straight line with a slope of one below pH 3. The $K_{D,SF\ CO2}$ value was determined by the above-mentioned procedure, assuming that the effect of the pressure on the K_{a1} value is negligibly small under the experimental conditions. The results are shown in Table 1 along with the K_D value of HMO_6Q between heptane and water. The $K_{D,SF\ CO2}$ values increased with an increase in the SF CO_2 pressure. The increase of the $K_{D,SF\ CO2}$ values should be ascribed to the increase of the density of SF CO_2.

A $K_{D,SF\ CO2}$ value at 20.4 MPa for HMO_6Q was about one tenth of the K_D for heptane - water system, indicating that the solubility of HMO_6Q in SF CO_2 is remarkably smaller compared with that in heptane.

The systematic study on the distribution behavior of chelating extractants is under way now.

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