Extraction Behavior of Gallium(III) with 2-Methyl-5-hexyloxymethyl-8-quinolinol and 5-Hexyloxymethyl-8-quinolinol from Weakly Acidic Solution into Supercritical CO$_2$ and Selective Separation of Gallium(III) from Aluminum(III)

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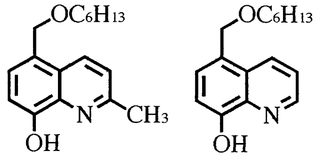
(Received August 13, 1997; CL-970635)

The extraction behavior of gallium(III) with 2-methyl-5-hexyloxymethyl-8-quinolinol (HMO$_6$Q) and 5-hexyloxymethyl-8-quinolinol (HO$_6$Q) (Figure 1) into supercritical CO$_2$ from weakly acidic solution was investigated. The extractability of gallium(III) is appreciably dependent on the temperature and pressure of supercritical CO$_2$. Gallium(III) was separated fairly selectively from aluminum(III) with HMO$_6$Q into supercritical CO$_2$.

Highly selective separation of metal ions has been one of the attractive fields in analytical chemistry, radiochemistry, and hydrometallurgy. Though the solvent extraction is the facile separation method for metal ions, most of the organic solvents used for solvent extraction are toxic. The waste organic solvents must be recovered from the ecological point of view.



HMO$_6$Q HO$_6$Q

Figure 1. Structures of alkylated 8-quinolinol derivatives.

More recently, supercritical CO$_2$ extraction has been one of the superior separation techniques because of easy removal of CO$_2$ from the extracted substances. In addition, CO$_2$ is characterized with its moderate critical constants (T_c = 31 ℃, P_c = 7.3 MPa). In spite of these advantageous characteristics, there have been only a few papers on the supercritical CO$_2$ extraction of metal ions from the aqueous solution.[1-4]

We previously reported that HMO$_6$Q and 2-butyl-5-hexyloxymethyl-8-quinolinol exhibited a high selectivity toward gallium(III) in a weakly acidic solution.[5]

In this work, the extraction behavior and the selective separation of gallium(III) from a weakly acidic solution with HMO$_6$Q and HO$_6$Q into supercritical CO$_2$ were invetigated.

HMO$_6$Q and HO$_6$Q were prepared as reported in our previous paper.[5] All the other chemicals used were of analytical reagent grade. All supercritical CO$_2$ extractions were carried out with the apparatus composed of the syringe pump (Isco, Model 500 D), the pump controller (Isco, Series D), and the 100-ml high-pressure stainless steel view cell. The extraction procedure is as follows: A 5 ml of 1.43 x 10^{-4} M gallium(III) perchlorate solution containing 0.1 M (H,Na)ClO$_4$ and 5 ml of 0.01 M HMO$_6$Q (HO$_6$Q) in heptane (5.0 x 10^{-2} mmole) were taken into different 5 ml-beaker placed in the cell. Since HMO$_6$Q is an oily liquid, it is difficult to take precisely a small amout of HMO$_6$Q into the cell. Therefore, HMO$_6$Q dissolved in 5 ml of heptane was used. In the case of HO$_6$Q, solid HO$_6$Q (5.0 x 10^{-2} mmole) was also supplied to the supercritical extraction of gallium(III). The syring pump was filled with CO$_2$ (99.99% purity) from a liquid-CO$_2$ cylinder and then pressurized by the pump controller. The pressurized liquid CO$_2$ was introduced into the preheated cell. The extraction was performed without stirring the aqueous solution of gallium(III). (static extraction). After 60 min, the outlet valve was opened while passing the pressurized CO$_2$ gas to the cell. The extraction cell pressure was monitored by a pressure monitor (Toyo Sokki). The temperature of the extraction cell was controlled within $\pm$0.2 ℃ by a temperature controller. The percentage extraction and the distribution ratios were calculated from the gallium(III) concentration in an aqueous phase before and after the extraction. Gallium(III) was analysed by plasma atomic emission spectrophotometry. The pH adjustment was made using perchloric acid solution. After extraction, the pH of the aqueous phase[6] in contact with 1 atm (0.10 MPa) atmosphere at 25 ℃ was immediately measured. The pH change before and after extraction was within 0.02 pH unit.

The extraction equilibrium was attained at the static extraction time of 40 min under the pressure of 9.1 MPa for HMO$_6$Q system and of 8.4 MPa for HO$_6$Q system at 50 ℃. These results illustrate that the extraction of gallium(III) with these extractants into supercritical CO$_2$ is fast compared with the solvent extraction using heptane, for the extraction equilibrium of gallium(III) with 0.01 M of these extractants into heptane was

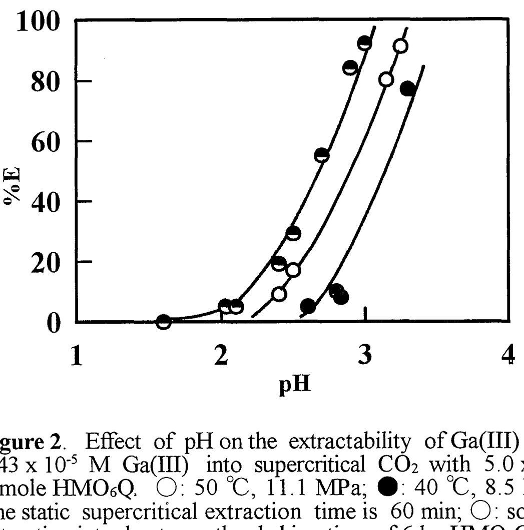


Figure 2. Effect of pH on the extractability of Ga(III) with 1.43 x 10^{-5} M Ga(III) into supercritical CO$_2$ with 5.0 x 10^{-2} mmole HMO$_6$Q. ○: 50 ℃, 11.1 MPa; ●: 40 ℃, 8.5 MPa. The static supercritical extraction time is 60 min; ○: solvent extraction into heptane, the shaking time of 6 h. HMO$_6$Q was dissolved in heptane.

attained in the pH range of 1.5 - 3.0 by shaking for at least 6 h at 25 ℃.[5]

The effect of pH on the supercritical $\mathrm{CO_2}$ extraction of gallium(III) with $\mathrm{HMO_6Q}$ dissolved in heptane was examined under the conditions of 50 ℃, 11.1 MPa and of 40 ℃, 8.5 MPa. The results were shown in Figure 2 along with that for the solvent extraction using heptane. Thus, the pH-percentage extraction curves for the supercritical $\mathrm{CO_2}$ extraction are very similar to that for the solvent extraction. The extraction curve obtained at 40 ℃ and 8.5 MPa shifted to the higher pH region than that at 50 ℃, 11.1 MPa. The effect of the pH on the supercritical $\mathrm{CO_2}$ extraction of gallium(III) with $\mathrm{HO_6Q}$ dissolved in heptane was also examined at 50 ℃. Gallium(III) was extracted from more acidic region at 11.1 MPa than at 8.4 MPa. Under the conditions of 50 ℃, 11.1 MPa, gallium(III) was extracted with $\mathrm{HO_6Q}$ dissolved in heptane from a lower pH region than with $\mathrm{HMO_6Q}$ dissolved in heptane. As reported in previous paper, the pH-percentage curve for the solvent extraction of gallium(III) with $\mathrm{HO_6Q}$ into heptane shifted to the lower pH region than that with $\mathrm{HMO_6Q}$.

The effect of the pressure of the supercritical $\mathrm{CO_2}$ on the extractability of gallium(III) with $\mathrm{HMO_6Q}$ dissolved in heptane was examined at 51 ℃ and 67 ℃ in the range of 9.0 - 14.0 MPa at pH 3.0. The results were shown in Figure 3. The extractability increases with an increament of the pressure. The similar result was obtained for the gallium(III)- $\mathrm{HO_6Q}$ system both in the presence and the absence of heptane at 60 ℃, pH 2.0. The extractability of gallium(III) with $\mathrm{HO_6Q}$ dissolved in heptane is smaller than that with $\mathrm{HO_6Q}$ in the absence of heptane under the same extraction conditions. This illustrates that heptane decreased the extractability of gallium(III). This may be related to the change of the characteristics of supercritical $\mathrm{CO_2}$ such as density by the addition of heptane. The detailed reasons are unclear.

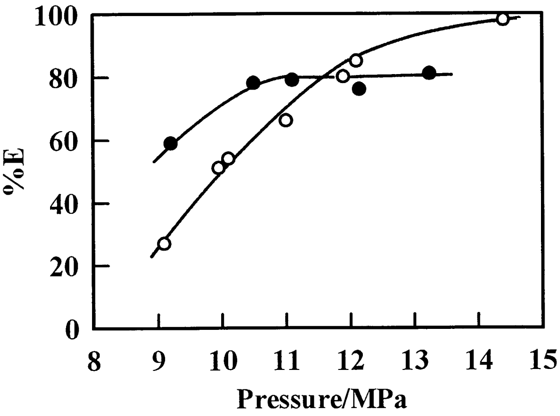


Figure 3. Efffect of the pressure of supercritical $\mathrm{CO_2}$ on the extractability of 1.43 x 10^{-5} M Ga(III) with 5.0 x 10^{-2} mmole $\mathrm{HMO_6Q}$ at pH 3.0. ●: 51 ℃ ; ○ 67 ℃. The other conditions are the same as in Figure 2.

The slope analysis was adopted for the determination of the composition of Ga(III)-$\mathrm{HMO_6Q}$ and Ga(III)-$\mathrm{HO_6Q}$ extracted into a supercritical $\mathrm{CO_2}$ phase. The plots of log D vs. log $(\mathrm{HMO_6Q})_{\mathrm{SF}}$ gave a straight line with a slope of 1.9, suggesting that two molecules of $\mathrm{HMO_6Q}$ participate in the supercritical $\mathrm{CO_2}$ extraction of gallium(III), where $(\mathrm{HMO_6Q})_{\mathrm{SF}}$ is the mass of $\mathrm{HMO_6Q}$ (mmole) in the supercritical $\mathrm{CO_2}$ phase. The extracted Ga(III)-$\mathrm{HMO_6Q}$ should be $\mathrm{Ga(OH)(H_2O)(MO_6Q)_2}$ as well as that extracted into heptane from a weakly acidic solution.[5] On the other hand, in the case of $\mathrm{HO_6Q}$, the slope of the log D vs. log $(\mathrm{HO_6Q})_{\mathrm{SF}}$ plots was ca.3, suggesting that the extracted Ga(III)-$\mathrm{HO_6Q}$ is $\mathrm{Ga(O_6Q)_3}$.

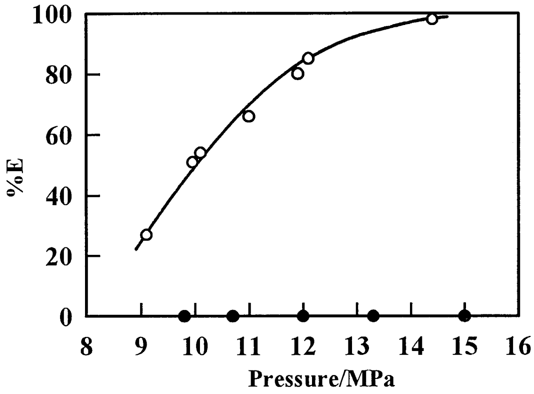


Figure 4. Separation of 1.43 x 10^{-5} M Ga(III) from 1.43 x 10^{-5} M Al(III) with 5.0 x 10^{-2} mmole $\mathrm{HMO_6Q}$ at 67 ℃ and pH 3.0. ○: Ga(III); ●: Al(III). The other conditions are the same as in Figure 2.

Figure 4 shows the separation effeciency of gallium(III) with $\mathrm{HMO_6Q}$ from aluminum(III) at pH 3.0 and 67 ℃. The extractability of gallium(III) increases with an increase of the pressure of supercritical $\mathrm{CO_2}$. More than 95% of gallium(III) was extracted at 15 MPa. On the other hand, aluminum(III) was not extracted at all in the range of 10.0 - 15.0 MPa. The separation of gallium(III) with $\mathrm{HO_6Q}$ from aluminum(III) was also investigated. Though above 10 MPa, more than 95% of gallium(III) was extracted, ca. 4% of aluminum(III) was also extracted. From these results, it is revealed that $\mathrm{HMO_6Q}$ is superior to $\mathrm{HO_6Q}$ for the mutual separation of gallium(III) into supercritical $\mathrm{CO_2}$.

The authors would like to thank Prof. H. Imura for valuable discussions and Mr. S. Mochizuki for experimental assistance. This work was supported by the Grant-in-Aid for Scientific Research from Ministry of Education, Science, Sports and Culture of Japan.

References and Notes

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