Quantitative extraction of aqueous alkali metal ions using supercritical carbon dioxide and polyethylene glycol ligands

Shunsuke Mochizuki, Richard L. Smith, Jr. and Hiroshi Inomata*

Department of Chemical Engineering, Research Center of Supercritical Fluid Technology, Tohoku University, Aoba-ku, Aramaki-Aza, Aoba 07, Sendai 980-8579, Japan. E-mail: inomata@scf.che.tohoku.ac.jp

Quantitative extraction (30–70%) of alkali metal ions (K^+, Na^+: 1.7×10^{-4} mol dm^{-3}) from aqueous solutions with supercritical carbon dioxide (40 °C, 10–18 MPa) could be achieved using glymes (triethylene glycol dimethyl ether (triglyme: 3G), tetraethylene glycol dimethyl ether (tetraglyme: 4G)) and the addition of pentadecafluoro-n-octanoic acid (HPFOA) that supplies a CO_2-philic counter ion and makes the metal–ligand complex soluble in the CO_2 solvent *via* counter ion exchange.

CO_2 in its supercritical state ($scCO_2$) is being proposed for many analytical and industrial applications. Although $scCO_2$ can dissolve many non-polar organic compounds,[1–3] it has difficulty in solubilizing metal ions due to its low relative permitivity. To address this, many researchers have examined the use of added ligands, surfactants or microemulsions. Some success in extracting transition metals such as Cu^{2+}, Pb^{2+}, Hg^{2+}, and lanthanoids, has been found using ligands (β-diketones, dithiocarbamates, organic phosphorus acids, *etc.*) *via* chelation,[4–6] but this technique seems unsuitable for alkali metals, since these do not form coordinate bonds with the above-mentioned ligands. Alkali metal ions, *e.g.* Na^+ or K^+, form complexes with only a few ligands, *e.g.* crown ethers or non-macrocyclic compounds such as surfactants having polyoxyethylene (POE) groups.[7–9] The polyethylene glycol compounds, glymes ($CH_3(OCH_2CH_2)_nOCH_3$), are attractive because of their ability to coordinate to metal ions. Darr *et al.* synthesized Ag^+(fluorinated-β-diketone)(glyme) complexes[10] and Pollard *et al.* examined Ce^{3+}(fluorinated-β-diketone)$_3$(glyme)[11] with the hope of obtaining $scCO_2$ soluble complexes. However, there are no reports of using glymes for extracting alkali metal ions with $scCO_2$.

In previous work, we developed a technique whereby alkali metal ions could be extracted with $scCO_2$, using an appropriate ligand with the addition of a small amount of additive that supplies a CO_2-philic counter ion.[12,13] The technique was applied to the extraction of Na^+ and K^+ using crown ether ligand and perfluorocarboxylic acid additive. Semi-quantitative (*ca.* 50%) recoveries were obtained. The perfluorocarboxylic acid additive made the metal ion–ligand complex soluble in $scCO_2$ by generating a CO_2-philic counter anion that exchanged with the anion of the metal–ligand complex. In this work, we report the experimental results on glymes, which are a new class of ligands that have not previously been identified as being applicable to alkali metal extractions with $scCO_2$ and which provide an inexpensive and practical alternative to crown ethers.

Materials NaCl (99.5%), KCl (99.5%), triethylene glycol dimethyl ether (triglyme: 3G, 93%), tetraethylene glycol dimethyl ether (tetraglyme: 4G, 98%), pentadecafluoro-n-octanoic acid (HPFOA, 95.0%) and HCl (analytical grade) were purchased from Wako Pure Chemical and used without further purification. The extraction apparatus used in this work has been previously described.[10] Briefly, an aqueous solution (6 ml) of the alkali metal salt (1.7×10^{-4} mol dm^{-3}; ionic strength (I) $= 1.0 \times 10^{-1}$ mol dm^{-3} (H, Cl)), a given amount of ligand and HPFOA (molar ratio; metal:ligand:HPFOA =

$1:30–300:30–300$) were loaded into an extraction cell (internal volume: 50 ml). The cell was immersed in a water bath (40 °C) and then pressurized by introducing CO_2 (99.9%). The solution in the cell was stirred by a magnetic stirrer for about 30 min to ensure complex formation and phase partitioning equilibrium. After equilibration, a vapor phase sample was taken by opening the stop valve and depressurizing. The extract in the vapor phase was trapped in a collection vessel that contained 10 ml of EtOH. After sampling, the residual aqueous phase in the cell was analyzed by HP 4500 ICP-MS to determine the metal ion concentration. The pH of the aqueous phase after extraction was also measured. The amount of metal in the collection vessel was analyzed to check the mass balance. The extraction recovery was determined by the difference in concentration of metal ions in the cell before and after extraction and was calculated by the following equation: Recovery = $([metal]_{init} - [metal]_{resid})/[metal]_{init}$, where $[metal]_{init}$ and $[metal]_{resid}$ represent the initial and residual concentration of metal ion in the cell, respectively.

Fig. 1 shows the extraction results for K^+ using 3G with $scCO_2$ at 40 °C. The recovery was negligibly small with only 3G, indicating that glymes may form complexes with K^+ but that their equilibrium constant is either very small or their solubility in $scCO_2$ is low. On the other hand, the addition of HPFOA gave a recovery that was between 10 and 20%. This can be explained by the fact that glymes form a complex with K^+, which has a low solubility in $scCO_2$. When HPFOA is added, the acid dissociates and gives a CO_2-philic $PFOA^-$ anion. The $PFOA^-$ anion undergoes exchange with the Cl^- anion of the complex in the aqueous phase, and consequently the affinity of the complex for $scCO_2$ increases due to the $scCO_2$-philic PFOA chain. This mechanism seems to be similar to that described in our previous work on crown ether ligands.[10,11] More importantly, the recoveries are semi-quantitative for this type of ligand. However, for the case of 3G, the recoveries were not as high as those obtained for the crown ether ligands, which could be attributed to the difference in the formation constants (K) between the alkali metal ion and glymes or crown ethers, those logarithmic values in MeOH at 25 °C were reported as 1.72 and 6.10, respectively.[14]

We examined the concentration dependence of HPFOA on the complex. The metal ion concentration ratio (D) between the
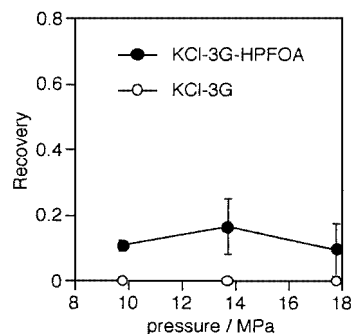

Fig. 1 Variation of recovery with pressure for K^+ using 3G. Extraction conditions: 40 °C, molar ratio; alkali metal:ligand = 1:100.
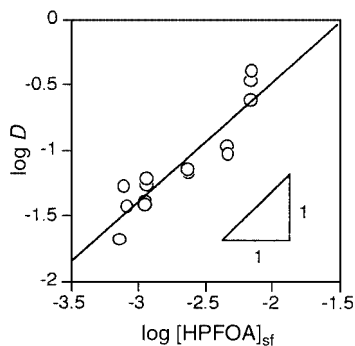
Fig. 2 Variation of log D with [HPFOA] using 3G. Extraction conditions: 40 °C, 13.7 MPa, molar ratio; alkali metal:ligand:HPFOA = 1:100:30–300.

Table 1 Recoveries (%) for alkali metal ions using 3G and 4G ligands and HPFOA additive. Extraction conditions: 40 °C, 13.7 MPa

Molar ratio[a]	Alkali metal	3G	4G
1:100:100	Na+	14.8	20.5
	K+	16.5	23.6
1:33:100	Na+	36.0	40.9
	K+	71.8	32.9

[a] Metal:glyme:HPFOA.

supercritical phase and aqueous phase was calculated from the data and plotted on a logarithmic scale against $[HPFOA]_{(sf)}$ for the KCl–3G–HPFOA system as shown in Fig. 2, where (sf) refers to species in the supercritical phase. The log D increased proportionally with an increase in $[HPFOA]_{(sf)}$ and its slope was found to be about unity, indicating that one HPFOA molecule took part in the extraction for each alkali metal ion–glyme complex. This trend is similar to that observed for extractions made with crown ether ligands in scCO$_2$.[13] However, when we plotted log D *versus* log [ligand] as in the previous work, a linear relationship was not obtained as shown in Fig. 3.
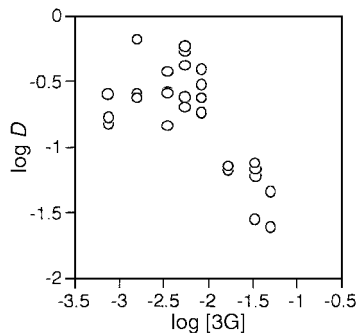

Fig. 3 Variation of log D with 3G concentration. Extraction conditions: 40 °C, 13.7 MPa, molar ratio; alkali metal:ligand:HPFOA = 1:30–300:100.

We considered that the range of ligand and additive concentrations studied might affect the observed recoveries. Since the ligand and additive concentrations were higher than that of the metal ions, strong HPFOA–glyme interactions in the liquid phase may occur. To check this, UV measurements of aqueous samples were made at 20 °C and atmospheric pressure. The spectra did not provide any evidence for HPFOA–glyme interaction. Another possibility is consecutive complex formation that might occur between alkali metal ion and glyme in aqueous phase such as 1:2 (metal:glyme), 1:3, *etc*. This would lead to a decrease in metal ion recovery since the larger complex would make ions unavailable for extraction if only the 1:1 complex was assumed to be extracted *via* counter ion exchange. Regardless of the solution interaction, at 3G concentrations of log [3G] from −2 to −2.7, the recovery increased remarkably up to around 80%.

We ran additional experiments with a longer oxyethylene chain glyme, 4G (see Table 1). Two molar ratios were considered at 40 °C and 13.7 MPa. At conditions of 1:100:100 (metal:glyme:HPFOA), recoveries were higher for K+ than Na+ for both glymes and it was found that 4G gave higher recoveries than 3G for the corresponding Na+ and K+ extractions. These results can be explained to some extent by the difference in complex formation ability. For the Na+–4G and K+–4G systems, the 1:1 (metal:ligand) formation constants (log K) in MeOH at 25 °C are 1.28 and 1.72, respectively.[14] However, when we changed the ligand concentration to 1:33:100, the recoveries did not follow the formation constant data. In conclusion, the molar ratios are not optimized for the highest recoveries, but with the use of glyme ligands and a CO$_2$-philic counter ion exchange technique, we demonstrate quantitative extraction. Our next step in this research is to perform more detailed measurements and to develop a model based on successive complex formation.

Notes and references

1 S. B. Hawthorne and D. J. Miller, *Anal. Chem.*, 1987, **59**, 1705.
2 J. J. Langenfeld, S. B. Hawthorne, D. J. Miller and J. Pawllszyn, *Anal. Chem.*, 1994, **66**, 909.
3 M. Johansson, T. Berglof, D. C. Baxter and W. Frech, *Analyst*, 1995, **120**, 755.
4 M. Ashraf-Khorassani, M. T. Combs and L. T. Taylor, *J. Chromatogr. A*, 1997, **774**, 37.
5 C. M. Wai and S. Wang, *J. Chromatogr. A*, 1997, **785**, 369.
6 J. M. Murphy and C. Erkey, *Environ. Sci. Technol.*, 1997, **31**, 1674.
7 S. Yanagida, K. Takahashi and M. Okahara, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1386.
8 A. M. Y. Jaber, G. J. Moody and J. D. R. Thomas, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1689.
9 D. C. W. Siew, R. P. Cooney, M. J. Taylor and A. J. Easteal, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 1109.
10 J. A. Darr, M. Poliakoff, A. J. Blake and W. Li, *Inorg. Chem.*, 1998, **37**, 5491.
11 K. D. Pollard, H. A. Jenkins and R. J. Puddephatt, *Chem. Mat.*, 2000, **12**, 701.
12 S. Mochizuki, N. Wada, R. L. Smith, Jr. and H. Inomata, *Anal. Commun.*, 1999, **36**, 51.
13 S. Mochizuki, N. Wada, R. L. Smith, Jr. and H. Inomata, *Analyst*, 1999, **124**, 1507.
14 G. Chaput, G. Jeminet and J. Jullard, *Can. J. Chem.*, 1975, **53**, 2240.