

SUPERCRITICAL CARBON DIOXIDE ENHANCED EXTRACTION OF METAL IONS IN AN AQUEOUS TWO-PHASE SYSTEM USING POLYETHYLENE GLYCOL

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ABSTRACT

Liquid-liquid extraction of metal ions in an aqueous two-phase system using aqueous solution of polyethylene glycol and sodium carbonate is experimentally studied to extend applicable metal species from TcO_4^- to RuO_4^{2-} and MoO_4^{2-} for nuclear waste treatment in nuclear energy application, and to MnO_4^- and CoO_2^- for recycling of raw materials of lithium ion batteries. Additionally, salting effect of using aqueous carbonate ions is experimentally investigated and use of high pressure carbon dioxide is discussed. As a consequence, the aqueous two-phase system using polyethylene glycol and sodium carbonate solution can be applied to extract not only TcO_4^- but also other anions of metal oxides for energy applications and high pressure carbon dioxide could be of use for salting.

INTRODUCTION

Aqueous two-phase systems have been used for partitioning of biological materials since the seminal work by P. Albertsson in Sweden, who developed the technique in the 1950s [1]. Its applicability has been greatly extended by R. D. Rogers in US to metal ions, especially radioactive pertechnetate [1-3], which was an important pioneering investigation for application in the treatment of nuclear wastes containing radioactive metal ions. Since chemical behaviour of pertechnetate is well known to be very similar to perrhenate, it was easy to extract perrhenate at the aqueous two-phase system using polyethylene glycol [4]. Our effort in the current study to extend the applicability of the technique is aiming at extending anions of metallic elements found in spent nuclear fuel for nuclear application or used materials for secondary batteries for more general energy application as well as discussing feasibility of high pressure carbon dioxide as a salting reagent for the aqueous two-phase system. For the first aim, the typical aqueous solution from nuclear fuel reprocessing may contain anions not only TcO_4^- but also MoO_4^{2-} and RuO_4^{2-} , which have limited solubilities of the waste contents in borosilicate glass that is world widely recognized media for vitrification of high level nuclear waste [5-6]. The solubilities of these two elements are so low in the borosilicate glass matrices that they may form separated phases in the vitrified glass and may cause degradation of the waste package. The final aim may be rationalized because liquefied or supercritical fluid of carbon dioxide is envisaged as a green solvent to reduce amount of secondary generating radioactive waste via the treatment and processing the nuclear wastes [7]. The authors have studied and successfully demonstrated application of supercritical carbon dioxide modified with tri-butyl phosphate to extract uranium, neptunium, plutonium, and americium from the real irradiated nuclear fuel in Japan [8-9], and in the current study we tried to combine the aqueous two-phase system with utilization of the high pressure carbon

dioxide with expecting its chemical effect as a salting reagent as well as its nature of green solvent.

MATERIALS AND METHODS

Chemicals and Experimental apparatus

An aqueous two-phase system composed of polyethylene glycol (PEG) as the polymer in water and water solution of inorganic salts was used in the current study. PEG-2000 was purchased from Wako Pure Chemical Industries, Ltd., Japan and used without further purification for the upper phase. The molecular formula weight ranged from 1800 through 2200 according to the product sheet given by the supplier. As inorganic salts, a mixture of ammonium sulfate and sodium carbonate or potassium carbonate was selected by taking account of phase separation from the upper phase and solubilities of the metal species. All inorganic chemicals are of reagent grade, and purchased from Wako Pure Chemical Industries, Ltd., Japan and used without any further purification.

Measurement of Distribution Ratios in the Ambient Pressure Experiments

A distribution ratio, D_M of each metal species, M is defined in this paper as the following equation:

$$D_M = \frac{C_{M,u}}{C_{M,l}}, \quad ! ! ! ! ! ! (1)$$

where $C_{M,u}$ is molar concentration of a metal species in the upper phase, i.e. PEG phase, and $C_{M,l}$ is that in the lower phase, i.e. phase of aqueous salt solution. The metal concentrations were measured by using an inductively coupled plasma spectrometer, ICPS-7000 (SHIMADZU, Japan) following hydrothermal decomposition of liquid samples of 0.03 cm³ from the both layers of the phases with using 0.15 cm³ concentrated nitric acid of reagent grade purchased from Wako Pure Chemical Industries, Ltd., Japan, in a fluoropolymer resin-lined acid digestion bomb of 23 cm³ in internal volume (model 4745, Nippon Genetics Corp. Ltd., Japan) and then diluted with ultrapure water produced by a Milli-Q Advantage A10 Ultrapure Water Purification System (Merk Millipore, Japan) in a chemical laboratory. The acid digestion was performed by keeping the bomb at 200°C for 3 hours in an electric furnace (Model HPM-2N, AZ ONE Corporation, Ltd., Japan).

Before sampling liquids from the two phase system, PEG-2000 was diluted by the ultrapure water up to 40% in weight and the aqueous salt solution where metal species was initially spiked are introduced in a test tube of 10 cm³ in volume and mixed well at 2000 rpm by a shaking incubator (Model SI-300, AZ ONE Corporation, Ltd., Japan) for liquid-liquid extraction at 40°C for 5 minutes. Just before sampling the mixture was centrifuged at 2000 rpm for 10 minutes using a centrifuge (Model H-103N, Kokusan, Japan). Before liquid-liquid extraction, concentrations of metal species were adjusted to 2.0×10⁻² mol dm⁻³ after the spike in the salt solution and the salt solution contained 2.5 mol dm⁻³ ammonium sulfate to accelerate phase separation. All inorganic salts and metal species were of reagent grade and commercially purchased from Wako Pure Chemical Industries, Ltd., Japan. In the case of investigating the salting effect by carbonate, potassium or sodium carbonate was added in the salt solution as well as metal species and ammonium sulfate.

Measurement of Distribution Ratios in High Pressure Experiments

A schematic diagram of apparatus is shown in Figure 1. The experimental system consisted of 1; a carbon dioxide gas cylinder, 2; a high-pressure syringe pump, 3; a

refrigerating machine, 4; a thermostatic water bath, 5; a high-pressure view cell for liquid-liquid extraction, 6; a pressure gauge, and 7 a magnetic stirrer. The cooling fluid of 278 K was circulated to the syringe pump (2) and the thermostatic water bath (5); the heating fluid of 313 K was circulated into the heating block of the high pressure view cell. A liquid-liquid extraction vessel of 60 cm³ in volume used has two view windows made of sapphire and the maximum durable pressure was 35 M Pa. In the first place, the aqueous solution to form the lower layer was introduced into the extraction vessel manually through the large inlet on the top of the vessel which is not illustrated in the figure and then all pressure seals and valves were tightly closed. The carbon dioxide of 99.999% purity contained in a gas cylinder purchased from Japan Fine Product, Japan was pressurized upto 15 MPa to introduce into the vessel by a syringe pumping system (ISCO Co. Ltd. Model 260D, USA) at 313 K. At this temperature and the pressure, carbon dioxide stays as supercritical fluid, because its critical temperature and pressure are 304 K and 7.4 MPa, respectively. The temperature of the vessel was kept at a given one by circulating water through the vessel funnel from a thermostatic water bath. The vessel was placed on a magnetic stirrer, and a fluoropolymer resin-coated magnetic bar was spinned remotely to mix the internal fluids. After adequate mixing of the upper and lower layer fluids, samples from each layer were taken from sampling lines installed in the upper and lower parts of the vessel. The concentrations of metallic species were determined as the same protocols described in the previous subsection. Through the sapphire windows, behavior of fluids; dispersion, coalescence, and formation of interface of the fluids were observed and recorded with a high definition camera with movie recording function(Canon Model EOS 70D, Japan).

A phase equilibrium analyzer for cloud point measurement (PEA-30) provided by Thar Design, USA was employed for solubility measurement of PEG-2000 in carbon dioxide. This device equips a volume changeable piston working with high pressure carbon dioxide, and is accurate than standard laboratory measurements due to precise control of sample volume, pressure and temperature.

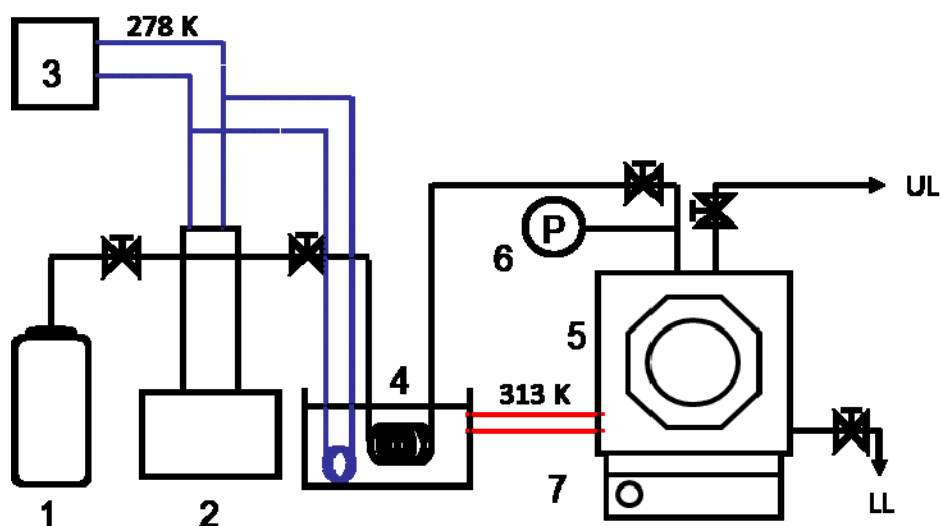


Figure 1: A schematic diagram of experimental set-up for high pressure carbon dioxide.

Dispersion Characterization

A 4.0 cm³ potassium carbonate solution of 2.0 mol dm⁻³ and 4.0 cm³ aqueous PEG-2000 solution of 20, 40, or 60 % in weight was separately introduced in three test tubes of borosilicate glass (Maruemu, Corp., NS-10, Japan) and shaken well at 2000 rpm by the shaking incubator at 313 K for one minute, and then a height of emulsion layer was pictured by the high definition camera and digitized to measure in cm as ΔZ . A time duration for coalescence of the emulsion into the two layers, Δt was also measured manually by a stopwatch. The similar experiments were performed using the high pressure vessel for the mixture of supercritical carbon dioxide, aqueous solution of PEG-2000, aqueous potassium carbonate solution at 313 K, and 15 MPa.

Since a dimensionless number introduced by R. A. Leonard has been recognized as a simple but universal modulus to characterize liquid-liquid dispersion in practical contactors for various conditions [12,13], N_{Di} defined by the following equation was evaluated in the current study.

$$N_{Di} = \frac{1}{t_R} \sqrt{\frac{\Delta Z}{a}}, \quad (2)$$

where, a is acceleration on coalescence dispersion or gravity constant, t_R is the average residence time in the coalescing dispersion band within the separating zone of a flowing system or the time to break in the test tube, and ΔZ is the thickness of the dispersion band in the separating zone of a liquid-liquid dispersion system or the initial thickness of the dispersion in the test tube.

RESULTS AND DISCUSSION

Distribution of Ru and Mo in the Aqueous two-phase System

In the first place, in order to confirm that the experimental protocols described in the subsection of materials and methods work, we extracted chromium as anionic ion CrO_4^- as an example. The phase separation of the aqueous two phase system using PEG-2000 and distribution of chromium was shown in **Figure 2**. The measured distribution ratio was 0.713 in this case applying the protocols described in the subsection.

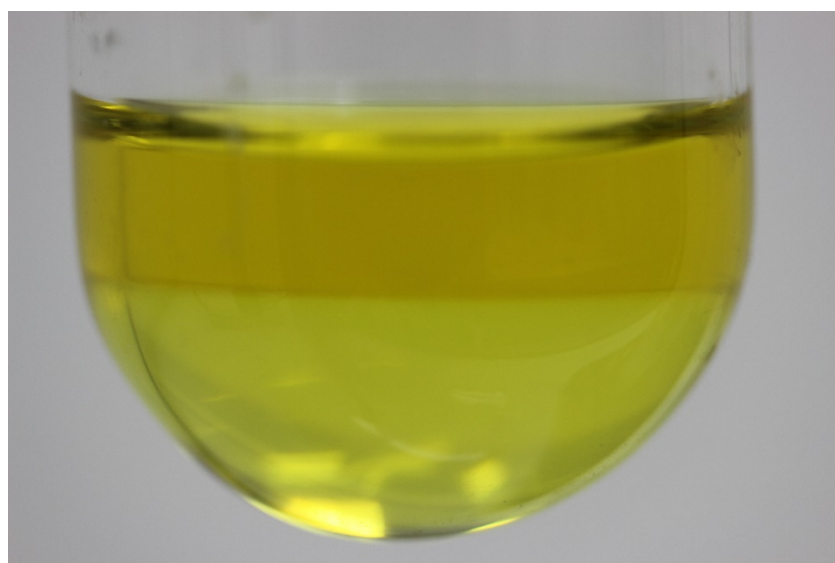


Figure 2 : A photograph for the distribution of CrO_4^- in the aqueous two-phase system. The upper layer was PEG-2000 rich phase, and the lower layer was salt solution initially contained potassium chromate and ammonium sulfate and 2mol dm⁻³ nitric acid.

By applying the same protocols, we determined the distribution ratios of ruthenium anion, RuO_4^{2-} , but the anion of ruthenium formed black solid and did not form aqueous solution. This is because RuO_4^{2-} is stable only in basic solution[10-11]. Then the lower phase was prepared as alkaline solution of 2.0 mol dm^{-3} sodium hydroxide. Since according to our trials, acid or alkaline solutions of greater than 8 mol dm^{-3} HNO_3 , HCl , or NaOH in molarity did not form aqueous two phase system with PEG-2000, we have selected the concentration of the 2.0 mol dm^{-3} NaOH for RuO_4^{2-} as a result of trade-off between basicity required for the stability of ruthenium species and two phase separation. The obtained distribution ratio was 0.044. This value is not so large being compared even with CrO_4^- but when we could set a large phase ratio in an extraction process, still we can recover ruthenium, and naturally the selectivity among other fission products should be evaluated and discussed in future.

Concerning with MoO_4^{2-} , we have selected also the concentration of the 2.0 mol dm^{-3} NaOH with the same reason as is with RuO_4^{2-} . The obtained distribution ratio was 0.499. This value seems more feasible for quantitative recovery by applying multistage extraction system already used in the nuclear industries.

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Distribution of Co and Mn in the Aqueous two-phase System

Distribution ratios of CoO_2^- and MnO_4^- were evaluated at acidic (2.0 mol dm^{-3} HNO_3 solution) solution. The selection of the acidity was based on the trade-off between pH required for the stability of metal species and two phase separation, and as same as in the Ru or Mo species. Compared with the ruthenium ion, determined distribution ratios of cobalt and manganese were larger, and 0.098 and 1.08 respectively, then these elements are also possible to extract in the two phase system with PEG-2000 for the recycling of raw materials of used lithium ion batteries after the extraction conditions are optimized through further works.

Salting Effects by CO_3^{2-} in Aqueous Phase at the ambient Pressure

By an addition of sodium carbonate in the lower layer, distribution ratio of perrhenate increased even with no addition of ammonium sulfate as is illustrated in **Figure 3**, and salting effect of carbonate ions were confirmed.

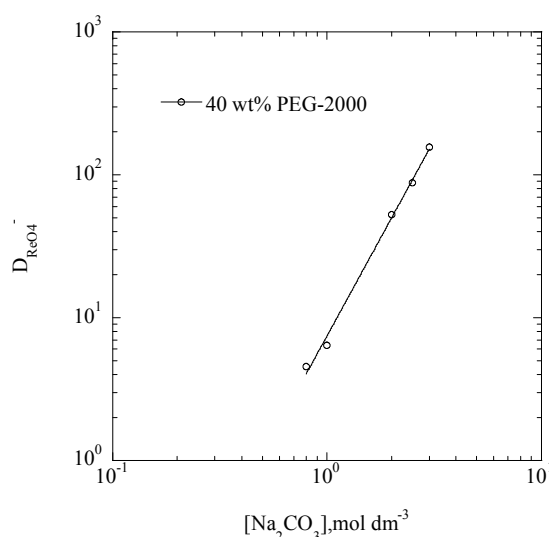


Figure 3. Salting effect by carbonate ion observed in the experiments at the ambient pressure.

Distribution behavior of Re with High Pressure Carbon Dioxide

When the aqueous two-phase system with PEG was pressurized with carbon dioxide, carbon dioxide was dissolved partially in the aqueous phase according to its solubility in water, 6% in weight at at 313 K, and 15 MPa. which is equivalent to 1.4 mol dm^{-3} and then may lead to salting markedly. On the other hand, PEG was also partially dissolved in high pressure carbon dioxide. A pressure – concentration diagrams measured in this study for PEG-2000 is illustrated in **Figure 4**.

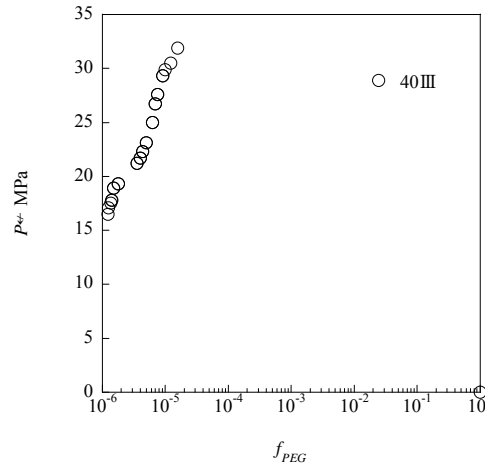


Figure 4 : A measured plot of pressure vs. molecular fractions of PEG 2000 in its mixture with carbon dioxide.

As is shown in **Figure 4**, in our experimental conditions at 313 K (40 °D) and 15 MPa, the PEG-2000 transferred to the high-pressure CO_2 phase was a small fraction, then only anti-solvent effect on the upper aqueous phase should be discussed in the future study. Experimentally, however, the three phase mixture of water, PEG, and CO_2 included a tiny micelle like dispersion, and distinct enhancement of distribution ratios have not ever measured in the current study. Obviously we should improve experimental protocols.

Dispersion Characteristics at the ambient pressure

A typical result of a series of experiment for decay of emulsion height by coalescence is illustrated in **Figure 5**.

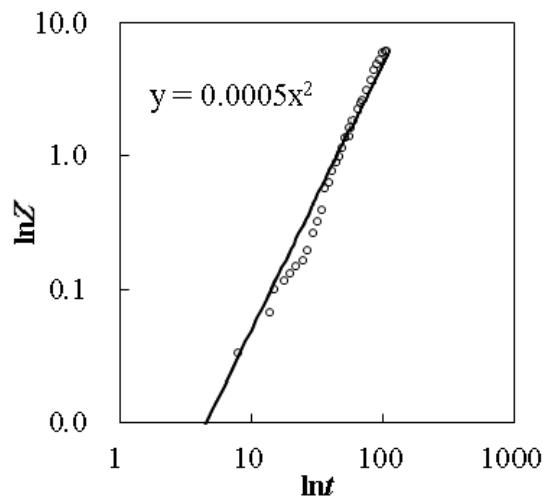


Figure 5: A Relationship between a band height of emulsion ΔZ and t by coalescence for 40% PEG

Table1 shows dispersion numbers evaluated in the current study for various content of the PEG-2000 in the upper phase. The dispersion number can directly give compatibility with a centrifugal contactor. i.e. a modern extractor using turbulent Couette flow between rotating concentric cylinders with a centrifugal settler applicable nuclear fuel reprocessing, and in terms of acceptability for the dispersion number 2×10^{-4} is a criteria for poor settling; 4×10^{-4} , fair settling, 8×10^{-4} good settling according to the literature [13].

Table1. Evaluated dispersion number on PEG-2000 content

PEG-2000 content, weight %	Z/t^2	\sqrt{Z}/t	$N_{Di}(\times 10^{-4})$
20	0.00041	0.020	6.5
30	0.00035	0.019	6.0
40	0.00045	0.021	6.8
50	0.00049	0.022	7.1
60	0.00065	0.026	8.1

Dispersion Characteristics with the High Pressure Carbon Dioxide

A similar experimental result was obtained for the dispersion number at high pressure experiment, and a value of 11×10^{-4} was evaluated in the case of 40% PEG-2000 in the upper phase of the aqueous two phase system. This result implies that acceptability of the aqueous two phase system with PEG and carbonated salt may be better with the effect by high pressure carbon dioxide.

CONCLUSION

Liquid-liquid extraction of metal ions in an aqueous two-phase system using aqueous solution of polyethylene glycol (PEG) and sodium or potassium carbonate is experimentally studied, and we obtain extension of applicable metal species from TcO_4^- to RuO_4^{2-} and MoO_4^{2-} for nuclear energy application, and to MnO_4^- and CoO_2^- for recycling of raw materials of lithium ion batteries. Additionally, salting effect using carbonate solution is confirmed which probably leads to application of high pressure carbon dioxide. On the other hand, we need further investigations on quantitative influence of fine creaming phase in the aqueous two phase system and anti-solvent effect of carbon dioxide on the PEG phase.

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