Two-Phase Extraction of Metal Ions Using a Water-Acetonitrile-Ethyl Acetate Ternary Mixed-Solvent Separation System

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A ternary mixed-solvent solution of water-acetonitrile-ethyl acetate changes from a homogeneous (single-phase) to a heterogeneous (two-phase) system with temperature and/or pressure changes. In this study, we used this system in a batch vessel to extract metal ions. Water-acetonitrile-ethyl acetate at a volume ratio of 3:8:4 containing 8-hydroxyquinoline was used as a ternary mixed-solvent solution, changing from homogeneous at 25°C to heterogeneous after 30 min at 0°C. The two-phase system comprised an upper (organic solvent-rich) phase and a lower (water-rich) phase at a volume ratio of 6:1. Fe(III), Co(II), and Ni(II) were used as model metal ions dissolved in the homogeneous solution at 25°C. The distribution constants and the extraction percentages were determined by measuring the metal ion concentrations in the upper and lower phases with inductively coupled plasma atomic emission spectroscopy. The metal ions were extracted through complexation with 8-hydroxyquinoline in the organic-rich phase with distribution constants and extraction percentage values, respectively, of 0.47 and 74 for Fe(III), 0.15 and 47 for Co(II), and 0.08 and 32 for Ni(II).

(Received March 12, 2013; Accepted April 20, 2013; Published June 10, 2013)

Introduction

The phase separation of aqueous systems containing polymers, micelles, and ionic liquid solutions has been well known, and used in the fields of analytical chemistry and separation science since the last century. For example, aqueous micellar solutions of some non-ionic surfactants separate into two distinct phases when heated above a certain temperature (the cloud point); that is, a temperature-induced phase separation occurs. One phase is an almost micelle-free aqueous solution (the aqueous phase), while the other is a concentrated surfactant solution containing considerable amounts of water (the surfactant-rich phase). Hydrophobic compounds dissolved in the aqueous micellar solution are extracted into the surfactant-rich phase, while hydrophilic compounds remain in the aqueous phase.

Fluorous chemistry, which can undergo phase separation, has been heavily investigated since the seminal work of Horváth and Rabai in 1994. Two-phase separation of fluorous-organic solvent mixed solutions has been applied in separation science. Mixed solutions of fluorous-organic solvents separate into two distinct phases in a batch vessel when cooled below a certain temperature, with the lower phase comprising an almost pure fluorous solvent, while the upper phase comprises an organic solvent. Based on this two-phase system, liquid-liquid and liquid-solid extractions have been reported using a variety of fluorous solvents.

A novel two-phase separation system involving ternary mixed solvents has been reported by our group. A ternary mixed solvent solution of water-hydrophilic/hydrophobic solvents changes from a homogeneous (single-phase) to a heterogeneous (two-phase) system with temperature and/or pressure changes. This phenomenon causes a specific fluidic behavior in a microspace, such as a microchannel on a microchip or a capillary tube, leading to new types of open-tubular capillary chromatography and microreactors. In this study, for the first time we have used a two-phase separation system comprising a ternary mixed-solvent solution in a batch vessel to extract metal ions.

Experimental

Water was purified with an Elix 3 UV system (Millipore Co., Billerica, MA). All reagents were obtained commercially, and were of analytical grade. Acetonitrile and ethyl acetate were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). 8-Hydroxyquinoline (8-HQ), iron (1000 ppm, 0.275 M HNO₃), nickel (1000 ppm, 0.1 M HNO₃), and cobalt (1000 ppm, 0.1 M HNO₃) standard solutions were purchased from Nacalai Tesque, Inc. (Kyoto, Japan).

A homogeneous ternary mixed-solvent solution of water-acetonitrile-ethyl acetate (at a volume ratio of 3:8:4) containing 8-HQ was prepared at 25°C. The metal ions were dissolved in the homogeneous solution, and the solution was then cooled to 0°C and held to obtain a heterogeneous solution including upper (organic solvent-rich) and lower (water-rich) phases. The metal concentrations were determined in both phases. Each phase was subjected to evaporation, and the resultant residue was dissolved in 0.1 M nitric acid (10 mL) for inductively coupled plasma atomic emission spectroscopy (ICP, 8100-Type instrument, Shimadzu Co.). Distribution constants (D) and extraction percentages (E%) were calculated using the following equations:
\[ D = C_o / C_w, \]

\[ E(\%) = 100 \frac{D}{D + V_w / V_o}, \]

in which \( C_o \) and \( C_w \) are the metal concentrations in the upper and lower phases, respectively; \( V_o \) and \( V_w \) are the volumes of the upper and lower phases, respectively.

**Results and Discussion**

*Phase diagram and tie line*

The phase diagram of the ternary mixed solvent solution of water-acetonitrile-ethyl acetate is shown in Fig. 1. The solid curve indicates the boundary between the heterogeneous and homogeneous systems at 25°C. The dotted curve is the boundary between these systems at 0°C. The plot (○) near the boundary curve at 25°C locates the component volume ratio of 3:8:4 for water-acetonitrile-ethyl acetate. The tie-line of the plot at 0°C on the phase diagram was constructed using the solvent composition of the homogeneous solution at 25°C, the water content of the lower phase in the batch vessel at 0°C (where Karl Fischer moisture titrator (MKC-610; API Co.) was used), and the boundary curve at 0°C. The volume ratio of the upper and lower phases at 0°C in the batch vessel corresponds to the ratio of the line lengths, which are separated by the plotted point on the tie line. In this case, the volume ratio of the upper and lower phases was 6:1, as shown in Fig. 1. The phase diagram of the ternary mixed solvent solution containing 10-mM 8-HQ was similar to that shown in Fig. 1, although 10-mM 8-HQ was only sparingly dissolved in a mixed solvent solution containing water at less than ca. 50 vol%.

**Preliminary extraction experiments**

Two preliminary experiments (Experiments 1 and 2) are illustrated in Fig. 2. In Experiment 1, a solution of ethyl acetate containing 10 mM 8-HQ and an acetic acid solution (pH 2.8) containing 0.34 mM metal ions (at a volume ratio of 6:1; total volume 15 mL) in a batch vessel was held for 30 min without stirring. This system, as might be expected, consisted of two

![Fig. 1 Phase diagram of the ternary mixed-solvent solution comprising water-acetonitrile-ethyl acetate. The solid curve represents 25°C and the dotted curve represents 0°C. The component ratio of water-acetonitrile-ethyl acetate for the plotted point (○) is a 3:8:4 volume ratio. The straight line on the plot represents the tie line at 0°C.]

![Fig. 2 Illustration of extraction experiments in the batch vessel. The extraction conditions are described in detail in Experiments 1-3 in the text.](https://example.com/f2.png)
phases. The metal concentrations of the two phases were then measured with ICP. $D$ and $E$ (%) were both zero for all metal ions (Fe(III), Co(II), and Cu(II)). That is, Experiment 1 showed no extraction behavior for the metal ions under the conditions used. In Experiment 2, the same conditions were used as in Experiment 1, but the system was well stirred in the batch vessel for 30 min, and then held without stirring for 30 min. The metal concentrations in the two phases were then measured by ICP. The $D$ and $E$ (%) values were, respectively, 0.46 and 73 for Fe(III), 0.15 and 47 for Co(II), and 0.08 and 32 for Ni(II) (the numbers were averages for 3 – 5 times measurements). Thus, as a general result, Experiment 2 showed extraction behavior for the metal ions. After 3 hours of stirring, $D$ and $E$ (%) remained constant at the above values for all metal ions.

**Extraction experiment using the ternary mixed solvent solution**

Experiment 3 using the ternary mixed solvent solution was carried out as illustrated in Fig. 2. A homogeneous ternary mixed solvent solution of water-acetonitrile-ethyl acetate (volume ratio 3:8:4; total volume 15 mL) containing 10 mM 8-HQ and 0.34 mM metal ion solution in a batch vessel was cooled from 25 to 0°C, and held for 30 min. The metal concentrations of the two phases were then measured by ICP. $D$ and $E$ (%) were, respectively, 0.47 and 74 for Fe(III), 0.15 and 47 for Co(II), and 0.08 and 32 for Ni(II) (the numbers were averages for 3 – 5 times measurements). That is, the two-phase system of the ternary mixed solvent solution performed similarly to the extraction system of Experiment 2. After 3 hours, $D$ and $E$ (%) remained constant at the above values for all metal ions. It is worth emphasizing that Experiment 3 using the two-phase system performed metal ion extraction with 8-HQ without stirring at almost the same $D$ and $E$ (%) values and those obtained in Experiment 2, although the extraction conditions, such as the pH values of the water-rich phase, have to be examined in detail in order to improve the extraction efficiency. The order of extraction performance obtained with 8-HQ in Experiments 2 and 3, Fe(II) > Co(II) > Ni(II), was consistent with that reported previously.23,24

**Extraction of mixed metal ions**

Mixtures of metal ions containing Fe(III) and Co(II), Fe(III) and Ni(II), and Co(II) and Ni(II) were extracted in the same way as in Experiment 3 (each metal concentration was 0.18 mM). The values of $D$ and $E$ (%) for the Fe(III) and Co(II) mixture were, respectively, 0.40 and 70 for Fe(III); 0.14 and 45 for Co(II). For the Fe(III) and Ni(II) mixture the respective $D$ and $E$ (%) values were 0.33 and 66 for Fe(III) and 0.08 and 32, for Ni(II). Finally, the respective $D$ and $E$ (%) values for the Co(II) and Ni(II) mixture were 0.16 and 50 for Co(II) and 0.11 and 39 for Ni(II) (the numbers were averages for 3 – 5 times measurements). These values for the metal ions were very similar to those obtained in Experiments 2 and 3.

**Conclusions**

A two-phase separation system comprising a ternary mixed-solvent system was reported. The water-acetonitrile-ethyl acetate system changed from a homogeneous (single-phase) to a heterogeneous (two-phase) system with temperature and/or pressure changes. In this study, for the first time, we used a two-phase separation system comprising a ternary mixed solvent solution in a batch vessel to extract metal ions. Model metal ions of Fe(III), Co(II), and Ni(II) were successfully extracted with the two-phase system. The experimental data obtained here suggest that the new phase separation system offers new capabilities in separation science, similar to other two-phase systems consisting of polymers, micelles, ionic liquids, and fluorous solutions.

**Acknowledgements**

This work was supported by a Grant-in-Aid for Scientific Research (C) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. It was also supported by “Advanced Study for Integrated Particle Science and Technology”, Strategic Development of Research Infrastructure for Private Universities, the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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