

令和 6 年 9 月 9 日現在

機関番号：82110

研究種目：研究活動スタート支援

研究期間：2022～2023

課題番号：22K20487

研究課題名（和文）New Malonamide Polyethoxylated Surfactant for Eco-friendly Ion Foam Flotation Process

研究課題名（英文）New Malonamide Polyethoxylated Surfactant for Eco-friendly Ion Foam Flotation Process

研究代表者

Micheau Cyril (MICHEAU, Cyril)

国立研究開発法人日本原子力研究開発機構・原子力科学研究部門 原子力科学研究所 物質科学研究センター・博士研究員

研究者番号：70961291

交付決定額（研究期間全体）：（直接経費） 2,200,000円

研究成果の概要（和文）：浮遊選鉱による金属イオン分離のための界面活性剤システムの研究開発を行なった。モデル界面活性剤を使用した粘土に関する浮遊選鉱研究では、3つの抽出メカニズム段階があることが明らかになった。これと並行して、モデル抽出剤を使用した溶媒抽出プロセスを研究した。金属イオンの選択性と速度に対して、凝集体生成の有無や配位構造の違い、金属イオン選択性や速度論に対して影響していることが明らかになった。

研究成果の学術的意義や社会的意義

It was found that size recognition effect of malonamide aggregates produced the ability to discriminate between metal ions. This discovery brings new conceptualization of extraction processes opening opportunities on molecules and processes developments, contributing to resource security in Japan.

研究成果の概要（英文）：This work aimed to develop a new surfactant system for the extraction and separation of metal ions using the flotation process. For this purpose, synthesis and characterization of a new malonamide polyethoxylated surfactant was considered. Unfortunately, a robust synthesis route couldn't be obtained due to external constraint. However, the characterization of reactants and model molecules were performed. A complete study of clay flotation using a surfactant model system was realized to characterize the flotation process. Technical feasibility of SANS experiments on foam has been demonstrated. Based on these results, three flotation processes were found depending on pH range. In parallel, NR measurement on malonamide model systems has been performed and had demonstrated the feasibility of analyzing liquid-air interfaces. These results highlighted new insights for liquid-liquid extraction processes deciphering the role of extractants aggregates on metal ion selectivity and kinetics.

研究分野：Soft matter, Separation process

キーワード：Flotation Malonamide Surfactant Foam Interface Solvent extraction SANS NR

様式 C - 19、F - 19 - 1 (共通)

1. 研究開始当初の背景

(1) Ion Foam Flotation (IFF) was firstly described in 1959 by F. Sebba in the frame of the mining industry, and focused on solid foams formation (froth). This process uses a surfactant molecule to concentrate and separate metal-ions at the gas-liquid (G-L) interface of an aqueous foam. Classical surfactants (SDS, CTAB) lead to the solid films, displaying a poor ionic selectivity, as metal ion extraction is governed by electrostatic interactions only.

(2) Malonamides have proven their efficiency in Liquid-Liquid Extraction (LLE) so far. Their selectivity is mainly driven by metal coordination but extractant aggregation seems to play a major role. However, G-L interface activity and aggregates structures remain unclear.

2. 研究の目的

In order to obtain a high metal-ion selectivity in the solvent free IFF process, it has been decided to develop a new selective system by grafting a malonamide function to a polyethoxylated alkyl chain, and simultaneously to elucidate interfacial mechanisms involved during metal-ion separation by studying IFF and LLE reference molecules.

(1) The creativity of the new system comes from the combination of coordination properties brought by the malonamide function, to foaming properties given by polyethoxylated chains. This new type of surfactant has never been synthesized.

(2) The characterization of reference molecules, will give new insights in term of physicochemical properties and extraction mechanisms involved during IFF and LLE, helping to develop innovative concepts for complex hydrometallurgical applications.

3. 研究の方法

(1) The first step was to synthesize novel malonamide grafted alkyl polyethoxylated surfactant. Two synthesis routes were envisaged starting from carboxylic acid surfactants (AKYPO®) such as esterification with hydroxyethyl malonamide, and peptide synthesis with malonamide function. Other routes with polyethylene glycol alkyl ether (CiEj) can be investigated using Brij® surfactant.

(2) In a second step, reference malonamide molecules used in the French nuclear fuel reprocessing cycle were selected, namely N,N,N,N -tetrahexylmalonamide (THMA) and N,N -dibutyl-N,N -dimethyl-2-tetradecylmalonamide (DBMA), as well as a model amine polyethoxylated surfactant, namely Ethoxylated (15) coco alkyl amine (Ethomeen), used in particle foam flotation process.

(3) The third step was to estimate the performance of the model molecules performing IFF and LLE experiments at the Marcoule Institute in Separation Chemistry (ICSM, France) with the help of Dr. P. BAUDUIN, Dr. O. DIAT and Dr. D. Bourgeois.

(4) In a fourth step, reference systems and phases were characterized in term of physicochemical properties through the use of various techniques, such as macroscopic foam analysis, zeta potential measurements, dynamic light scattering (DLS) measurements, interfacial tension (IFT) measurements, mainly performed at ICSM.

(5) Finally, the multi-scale structural characterization of the different systems was performed using the SANS-J instrument at JRR-3 facility (Tokai, Ibaraki), and the soft interface analyzer (SOFIA) on beamline 16 at J-PARC MLF (Tokai, Ibaraki), with the help of Dr. N. L. YAMADA and Dr. M. YAMADA from KEK, and Dr. K. AKUTSU from CROSS. The small angle X-ray scattering (SAXS) analysis was performed at ICSM,

This research method allowed to decipher the different physicochemical mechanisms involved during either IFF and LLE process and more specifically to correlate supra-molecular organization to extraction efficiency, selectivity and kinetic.

4. 研究成果

(1) The development of the new surfactant system for the extraction and separation of rare earth elements and/or platinum group metals using the IFF process was considered. For the synthesis, two main routes were planned: (i) esterification between the polyethoxylated carboxylic acid surfactant AKYPO LS-090 and the N(1),N(3)-Bis(2-hydroxyethyl)malonamide, and (ii) alkylation between malonamide molecule and the polyethoxylated alcohol surfactant Brij 010 (or Brij S10). Unfortunately, delay and unavailability of some reactants drastically impacted the original plan, compromising the obtention of a robust synthesis route and the obtention of the desired product with a reasonable purity. In this way, additional synthesis routes are being considered in order to reduce reactant cost and synthesis steps. However, the three received surfactants (AKYPO LS-090, Brij 010 and S10) were characterized in terms of purity, pKa and micelle surface charge.

(2) Ethomeen surfactant system was investigated as a reference polyethoxylated surfactant molecule for the flotation of nano-clay particles (Laponite RD) in the context of soil and ground water contamination by heavy metals and radionuclides. For this study, a specific flotation column for small angle neutron scattering (SANS) analysis on foam was developed and successfully used at SANS-J, JRR-3, demonstrating the technical feasibility of measuring foam film thickness at the beamline. Due to the pH-sensitivity of the Ethomeen, flotation experiment of 1 g/L Laponite RD solution were performed as function of the pH at ICSM. Two recovery regimes of the clays were observed namely a total recovery under acidic ($\text{pH} < 6$) and neutral ($\text{pH} 6-10$) conditions, and an unexpected negative recovery under alkaline conditions ($\text{pH} > 10$). To elucidate the mechanisms involved in the particle flotation process for each of the pH conditions, the bulk and foam phases were analyzed using the combination of zeta potential measurements, DLS, foam image analysis and SANS. This multi-scale analysis method has revealed the existence of three flotation processes, as described in Figure 1:

surfactant foam fractionation at $\text{pH} > 10$ where the negatively charged Ethomeen molecules and the clay particles repelled each other at the air-liquid interfaces of the foam films; clay particle foam flotation at $\text{pH} 6-10$ with a total extraction of the clay which formed large aggregates with Ethomeen molecules through electrostatic attractive interactions, stabilizing the foam Plateau borders (i.e. film junctions); precipitate froth flotation at $2 < \text{pH} < 6$ with a total extraction of the clay which formed a gel with the surfactant leading to the formation of coarse foam. The findings obtained here provide important guidance for separating various particles using flotation

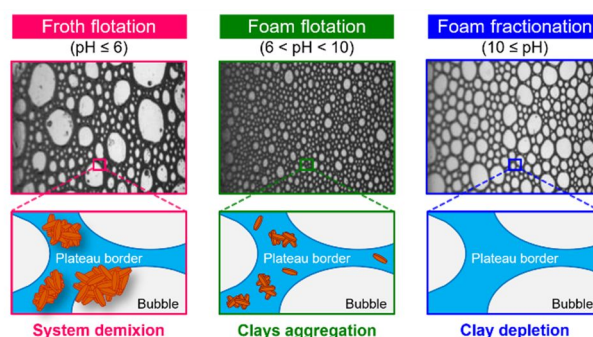


Figure 1: pH-dependent clay flotation regimes

such as for the separation of oppositely charged particles (i.e. ore and gangue), to recover sulfide minerals, or for the decontamination of mine water using nanometric sorbents. The findings obtained here are a good proof of concept demonstrating that this physicochemical method combined with multiscale structure analysis provides fundamental knowledge in foam and soft matter fields, such as surfactant/solutes interactions, foam and micelles structure, and their relationship helping to design new IFF processes. In addition, this process can be employed for the decontamination of radioactive elements due to accidental release in soil or groundwater and seawater, such as cesium or lanthanides ions, with lowering the volume of the nuclear wastes. Furthermore, the accumulated knowledge on foam properties can also be valuable for the development of foam decontamination technologies for radioactive surfaces.

(3) Reference malonamide extractant systems were investigated in the scope of LLE process for the separation and recovery of Palladium (Pd(II)) and Neodymium (Nd(III)). In this way, THMA in toluene system was compared to DBMA in *n*-heptane system. According to the extraction experiments performed at the ICSM, THMA in toluene has far higher affinity for Pd(II) than for Nd(III) during extraction from a 3 M HNO₃ aqueous phase compared with DBMA in the same diluent or in *n*-heptane in the

case of 0.3 M extractant concentration. However, for Pd(II), THMA has slower extraction kinetics. These unexpected solvent effects on selectivity and kinetics for both malonamide cannot be explained on the basis of classical coordination chemistry only. To elucidate the mechanisms involved in the LLE process using malonamide molecules, the organic bulk phases and G-L interfaces were analyzed using the combination of SAXS, IFT and neutron reflectivity (NR). It has thus been demonstrated that THMA in toluene forms small associates in the organic bulk phase and accumulates in a diffuse layer at the interface, decreasing Pd(II) coordination probability and resulting in slow extraction (see Figure 2a). DBMA in *n*-heptane forms large aggregates and a compact, dense interfacial layer, resulting in rapid Pd(II) and Nd(III) extraction (see Figure 2b). Thus, Pd(II) extraction is driven by interfacial coordination alone, whereas the incorporation of Nd(III) into the core of large aggregates governs Nd(III) extraction in the interfacial layer. These results suggest that the interface should be described as a nanoscale interphase containing a high extractant concentration compared with the organic bulk phase. This discovery is of great value as it is the first explicit demonstration of the influence of supramolecular assemblies on LLE extraction. In addition, NR measurement on malonamide standard systems performed at J-PARC, MLF, had demonstrated the feasibility of analyzing liquid-air interfaces. In the future, this research may lead to the development of solvent extraction technology from new perspectives, such as the design of metal ion separation systems that take into account the characteristics of supramolecular aggregates, and is expected to contribute to Japan resource security.

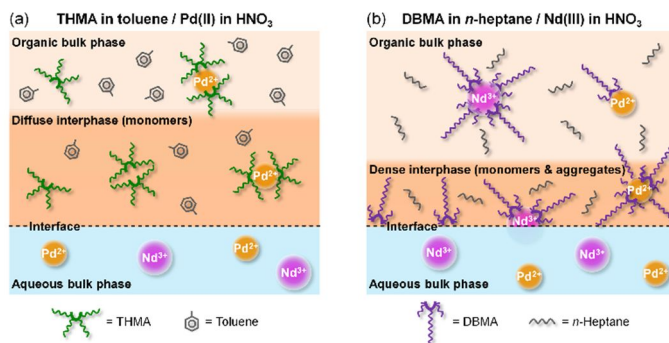


Figure 2: Supramolecular organization of (a) THMA in toluene and (b) DBMA in *n*-heptane

(4) Despite the fact that the new malonamide surfactant wasn't synthesized, analysis methodology, sample environment and experiments protocol at the JRR-3 reactor and J-PARC, MLF synchrotron were developed. This paves the way for future analysis using surfactant and extractant systems, and also for the characterization of the future malonamide polyethoxylated surfactant after it will be synthesized. In parallel, this study opened a new research plan through the development and improvement of LLE systems by using the power of supramolecular assemblies. In this way, research project to decipher the parameters that trigger aggregation and control the size of the aggregates, and thus the selectivity, are under investigation, in collaboration with the ICSM. Finally, this start-up work led to the publication of three articles in international peer reviewed journals (see references) as well as Japanese press release in 2024.

<引用文献>

. C. Micheau, Y. Ueda, K. Akutsu-Suyama, D. Bourgeois, R. Motokawa, Deuterated malonamide synthesis for fundamental research on solvent extraction systems, *Solvent Extraction and Ion Exchange*, 41 (2), 221-240 (2023)

. C. Micheau, Y. Ueda, R. Motokawa, P. Bauduin, L. Girard, O. Diat, Foam flotation of clay particles using a bifunctional amine surfactant, *Langmuir*, 39, 10965-10977 (2023)

. Micheau, Y. Ueda, R. Motokawa, K. Akutsu-Suyama, N. L. Yamada, M. Yamada, S. A. Moussaoui, E. Makombe, D. Meyer, L. Berthon, D. Bourgeois, Organization of malonamides from the interface to the organic bulk phase, *Journal of Molecular Liquids*, 401, 124372 (2024)

5. 主な発表論文等

〔雑誌論文〕 計3件（うち査読付論文 1件/うち国際共著 1件/うちオープンアクセス 0件）

1. 著者名 Micheau Cyril, Ueda Yuki, Akutsu-Suyama Kazuhiro, Bourgeois Damien, Motokawa Ryuhei	4. 巻 41
2. 論文標題 Deuterated Malonamide Synthesis for Fundamental Research on Solvent Extraction Systems	5. 発行年 2023年
3. 雑誌名 Solvent Extraction and Ion Exchange	6. 最初と最後の頁 221 ~ 240
掲載論文のDOI (デジタルオブジェクト識別子) 10.1080/07366299.2023.2166351	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

1. 著者名 Micheau Cyril, Ueda Yuki, Motokawa Ryuhei, Bauduin Pierre, Girard Luc, Diat Olivier	4. 巻 39
2. 論文標題 Foam Flotation of Clay Particles Using a Bifunctional Amine Surfactant	5. 発行年 2023年
3. 雑誌名 Langmuir	6. 最初と最後の頁 10965 ~ 10977
掲載論文のDOI (デジタルオブジェクト識別子) 10.1021/acs.langmuir.3c01213	査読の有無 無
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 -

1. 著者名 Micheau Cyril, Ueda Yuki, Motokawa Ryuhei, Akutsu-Suyama Kazuhiro, Yamada Norifumi L., Yamada Masako, Moussaoui Sayed Ali, Makombe Elizabeth, Meyer Daniel, Berthon Laurence, Bourgeois Damien	4. 巻 401
2. 論文標題 Organization of malonamides from the interface to the organic bulk phase	5. 発行年 2024年
3. 雑誌名 Journal of Molecular Liquids	6. 最初と最後の頁 124372 ~ 124372
掲載論文のDOI (デジタルオブジェクト識別子) 10.1016/j.molliq.2024.124372	査読の有無 無
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 -

〔学会発表〕 計1件（うち招待講演 1件/うち国際学会 1件）

1. 発表者名 Cyril Micheau
2. 発表標題 Deuterated malonamide synthesis to probe interfacial mechanisms involved in solvent extraction process
3. 学会等名 Deuterium Science Entering a New Phase (J-PARC Workshop) (招待講演) (国際学会)
4. 発表年 2023年

〔図書〕 計0件

〔産業財産権〕

〔その他〕

-

6. 研究組織

	氏名 (ローマ字氏名) (研究者番号)	所属研究機関・部局・職 (機関番号)	備考
--	---------------------------	-----------------------	----

7. 科研費を使用して開催した国際研究集会

〔国際研究集会〕 計0件

8. 本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関
---------	---------