アカデミックプログラム［Ｂ講演］｜22. 資源利用化学・環境・グリーンケミストリー：口頭Ｂ講演

2024年3月18日(月) 13:00 ~ 15:30 A1455(14号館 [5階] 1455)

[A1455-1pm] 22. 資源利用化学・環境・グリーンケミストリー

座長：吉川 聡一、大嶋 孝志

英語
13:00 ~ 13:20
[A1455-1pm-01]
ホルモース反応ネットワークの構造理解を通した反応選択性の制御

○西島 弘晃[1]、近谷 元大[1]、石原 菜々子[1]、藤本 泰成[1]、田畑 裕[1]、長谷 陽子[1,2]、中西 周次[1] (1. 阪大院基礎工、2. (株）豊田中央研究所)

英語
13:20 ~ 13:40
[A1455-1pm-02]
Multicomponent Adsorption Equilibria Modeling of Phenol and Ciprofloxacin on Differently Prepared Polyethylene Terephthalate Microplastics

○Christian Ebere Enyoh[1], Qingyue Wang[1] (1. Graduate School of Science and Engineering, Saitama University, Japan)

英語
13:40 ~ 14:00
[A1455-1pm-03]
ジアミンを二酸化炭素吸収材とする高効率Direct Air Capture

○曹 芙蓉[1]、吉川 聡一[1]、山添 誠司[1] (1. 東京都立大学)

日本語
14:00 ~ 14:20
[A1455-1pm-04]
ジアミンのCO_2吸脱着特性評価

○八木原 陸矢[1]、吉川 聡一[1]、山添 誠司[1] (1. 東京都立大学)

14:20 ~ 14:30
休憩

日本語
14:30 ~ 14:50
[A1455-1pm-05]
プルシアンブルー類似体を用いた水蒸気を含むガスおよび水中からのメタノール吸着

○首藤 雄大[1]、川本 徹[1]、高橋 顕[1] (1. 産業技術総合研究所)

日本語
14:50 ~ 15:10
[A1455-1pm-06]
作業環境測定での活性炭・シリカゲル捕集剤と有機溶剤抽出効率

○安彦 泰進[1] (1. 独立行政法人 労働者健康安全機構)

日本語
15:10 ~ 15:30

[A1455-1pm-07]

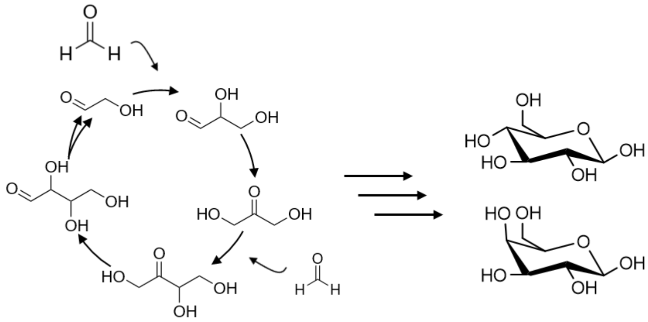
ヘテロジトピックレセプターを用いた塩化リチウムの選択的固-液抽出

○三室 翼[1]、平澤 学[2,1]、近藤 慎一[1] (1. 山形大理、2. レゾナック)

Controlling Reaction Selectivity through Understanding of the Formose Reaction Network

(1. Osaka Univ., 2. Toyota Central R&D Labs., Inc.) ○Hiroaki Nishijima[1], Genta Chikatani[1], Nanako Ishihara[1], Taisei Fujimoto[1], Hiro Tabata[1], Yoko Hase[1,2], Shuji Nakanishi[1]

Keywords: Formose reaction, Chemical Reaction Networks, Sugar, Autocatalytic Reaction, Artificial Photosynthesis



With global warming emerging as an urgent issue, the development of technologies to support the carbon cycle is becoming increasingly critical. In this context, the formose reaction, which allows for the non-enzymatic synthesis of sugars from formaldehyde (HCHO) — itself can be reductively formed from CO_2 — has attracted significant interest[1]. In the formose reaction, sugars are produced through a combination of three types of reactions: the aldol reaction, the retro-aldol reaction, and the Lobry de Bruyn–van Ekenstein transformation[2]. Although the parasitic Cannizzaro reaction that converts sugars into sugar alcohols lowers the yield of sugar production in the formose reaction, we have recently succeeded in developing an WO_4^{2-} catalyst that allows to suppress the Cannizzaro reaction[3]. Nevertheless, the efficiency of producing linear sugars, like glucose and fructose, remains low when employing this catalyst. The next challenge is to enhance the production selectivity of such linear sugars that are easily metabolized by living organisms. In this study, we propose a cascade-type reaction using two types of catalysts as one strategy to enhance the production efficiency of converting HCHO to metabolizable sugars. The design of such reaction systems can only be achieved through a comprehensive structural understanding of the complex networks involved in the formose reaction. More specifically, in the first stage, we employ a WO_4^{2-} catalyst to efficiently convert HCHO into C3 and C4 compounds, key reaction intermediates. Subsequently, in the second stage, NaOH catalyst was used to facilitate the production of sugars from these C3 and C4 compounds. In this cascade reaction system employing two different catalysts, it has been confirmed that products such as galactose, which are not obtainable using either WO_4^{2-} or NaOH catalysts alone, are produced.

1) J.B. García Martínez et al., *J.CO$_2$ Util.* **2021,** 53, 101726

2) A. M. Butlerow, *Compt. Rendus Acad. Sci.* **1861**, 53, 145 –147

3) H. Tabata, G. Chikatani, et.al., *Chem. Sci.* **2023**, 14, 13475-13484.

Modeling of Multicomponent Adsorption Equilibria of Phenol and Ciprofloxacin on Differently Prepared Polyethylene Terephthalate Microplastics

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Correspondence: cenyoh@gmail.com, ORCID ID: 0000-0003-4132-8988 (C.E.E); seiyo@mail.saitama-u.ac.jp, ORCID ID: 0000-0002-7673-2836(Q.W.)

Abstract

Multicomponent systems are representative of the most common real situations as many industrial discharges contain a mixture of several pollutants [1]. This study explores the concurrent adsorption of phenol (PHE) and ciprofloxacin (CIP) onto distinct polyethylene terephthalate microplastics (PET MPs)—pristine (Pr-PET), acid-modified (Mod-PET), and thermal-oxidatively aged (Ag-PET)—in a multicomponent solution. Employing the Extended-Langmuir (EL), Extended-Freundlich isotherm (EF), and a newly developed Artificial Neural Network (ANN) model, equilibrium adsorption capacities were predicted. Model parameters were estimated using the SOLVER error minimization technique in Microsoft Excel. The EL isotherm exhibited superior fitting for Pr-PET MPs and Ag-PET MPs, while EF excelled for Mod-PET MPs. Monolayer adsorption capacities for both PHE and CIP surpassed those of single-component adsorption. The developed ANN featured 3 hidden layers for Pr-PET MPs and Ag-PET MPs, and 5 hidden layers for Mod-PET MPs **(Figure 1)**, employing a hyperbolic tangent (Tanh) activation function. These models showcased impressive performance metrics, including R^2 (0.989-0.999), low Root Mean Square Error (RMSE) (0.001 – 0.413), and Average Absolute Error (AAE) (0.009 – 0.327) values. P-factor values below 1 indicated synergistic interactions in the binary system **(Figure 2)**. Selectivity ratio (S_R) values ranged from 0.136 for Pr-PET MPs to 0.256 for Ag-PET MPs for PHE, and from 3.902 for Ag-PET MPs to 7.361 for Pr-PET MPs for CIP. This disparity suggests PET MPs exhibit higher selectivity toward CIP than PHE. The study underscores the efficacy of developed PET MPs for binary adsorption of PHE and CIP in aqueous solutions.

Keywords: Artificial neural network, Machine learning, PPCPs, Separation, Selective adsorption, Synergistic interaction, Water treatment

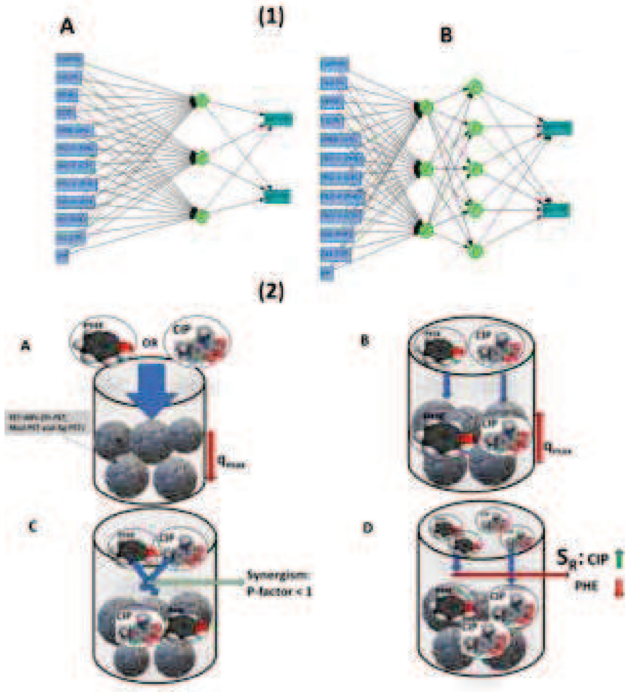


Figure (1). The developed ANN and (2) The graphical representation of the interactive effect of PHE and CIP in binary adsorption system to PET MPs adsorbent.

[1] Enyoh, C. E., & Isiuku, B. O. (2021). *Current Research in Green and Sustainable Chemistry*, 4, 100094. doi:10.1016/j.crgsc.2021.100094

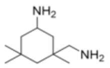
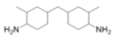
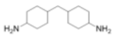
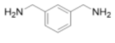
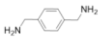
An efficient system for direct air capture utilizes diamine as sorbent.

(*Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University*) ○Furong Cao, Soichi Kikkawa, Seiji Yamazoe

Key Words: Carbon Dioxide; Direct Air Capture; Diamine; Phase Separation

The liquid–solid phase separation phenomenon exhibited a high removal efficiency for low concentration CO_2, which has potential for direct air capture (DAC).[1] In this work, a series of aqueous diamine solutions was screened for capturing 400 ppm CO_2. All amine loaded more than1 equilibrium CO_2, and white solid precipitates appeared in this system at the begging stage of CO_2 absorption (**Table 1**). In particular, isophorone diamine (IPDA) maintained >90% CO_2 removal from 400 ppm CO_2 for 726 min (T_{90} value), and the durability was highest among tested amines, and IPDA showed >99% CO_2 removal even under a 500 mL min^{-1}, in which the contact rate between CO_2 and IPDA aqueous solution and the CO_2 absorption rate reached 13,760 h^{-1} and 540 μmol h^{-1} $mol_{IPDA}{}^{-1}$, respectively (Figure 1). The CO_2 was captured in aqueous IPDA solution that 90% of the captured CO_2 could be recycled. The precipitate from IPDA was analyzed by ^{13}C NMR (164.85 and 161.23 ppm) and FT-IR (absorption bands at 1600-1660 cm^{-1}), revealing the structure of products as (isophorondiamine)carbamic acid and bicarbonate (HCO_3^-/CO_3^{2-}). Therefore, this work provides a foundation for establishing a solid–liquid phase change system for a highly efficient and environmentally friendly DAC system using aqueous solvent.

Table1. CO_2 adsorption properties of various diamines in aqueous solution for 400 ppm CO_2-N_2.

Entry	Amine	T_{90}/min	CO_2/mmol
1		726	1.03
2		65	1.09
3		27	1.26
4		2	1.07
5		441	1.28

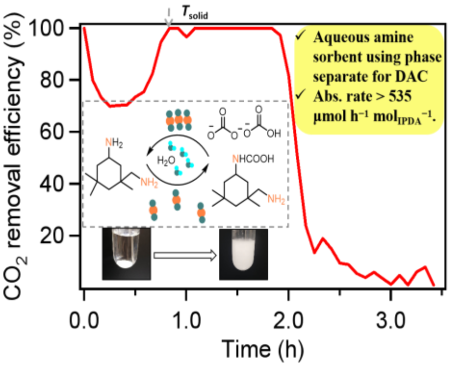


Figure 1. CO_2 removal efficiency over IPDA under 500 mL/min gas flow rates of 400 ppm CO_2. IPDA: 1 mmol; H_2O: 2 mL; (S_{abs} = 1.06).

1) (a) P. Luis *et. al.*, *Desalination* **2016**, *380*, 93−99. (b) X. Jin *et. al.*, *Sep. Purif. Technol.* **2022**, *298*, 120630. (c) S. Kikkawa *et. al.*, *ACS Environ. Au* **2022**, *2*, 354−362. (d) F. Inagaki *et. al.*, *J. Am. Chem. Soc.* **2017**, *139*, 4639−4642.

日本化学会 第104春季年会 (2024)

ジアミンの CO_2 吸脱着特性評価

（都立大院理）○八木原 陸矢・吉川 聡一・山添 誠司

Evaluation of CO_2 Absorption-Desorption Properties of Diamines

(*Tokyo Metropolitan University*) ○Rikuya Yagihara, Soichi Kikkawa, Seiji Yamazoe

Global warming and climate change are closely related to the rising concentration of CO_2 in the atmosphere. A large-scale CO_2 transport system is essential for CCUS technologies that enable to substantial reductions in carbon emissions. In typical, CO_2 is compressed into liquefied CO_2 or supercritical fluid and transported to consumption places by ship or pipeline[1]. However, these systems cost high energy to maintain the states and have safety issues[2].

Our group recently reported highly efficient CO_2 capture system accompanied with a liquid–solid phase change by using a DMSO solution of diamine with cyclohexyl group as a sorbent[3]. The carbamic acid was formed by capturing a molar of CO_2 per diamine molecule, and solid carbamic acid was precipitated simultaneously. Thus, highly efficient CO_2 absorption was achieved due to the low concentration of CO_2-absorbed diamine in the liquid phase. In this study, focusing on the chemical transport of CO_2, we investigate the CO_2 absorption capacity of various diamines and a DMSO solution of diamine can absorb 2 equimolar CO_2 to diamine under flowing certain concentration of CO_2 gas. Furthermore, the 1 equimolar CO_2 could be released under ambient temperature, and the captured CO_2 was perfectly released at 60 ℃. These results suggest the potential of a safer chemical transport system of CO_2 than existing systems using high pressure of CO_2.

Keywords：Carbon dioxide, Diamine, Carbamic acid, Chemical transportation, CCUS

大気中の CO_2 濃度は気候変動や地球温暖化と密接に関係しており，世界的に炭素排出量の削減が求められている．実質的な炭素排出を抑制する CCUS 技術において，CO_2 の大規模輸送技術は必要不可欠である．CO_2 は液化，または超臨界状態まで圧縮され，パイプラインや船舶で輸送される[1]．しかし，大容量の圧縮 CO_2 を扱うため，温度圧力の管理やタンクの設計開発，安全性などに課題が残る[2]．

我々は，CO_2 運搬技術としてアミンによる化学的輸送が有望と考えている．近年，シクロヘキシル環を有するジアミンを用いた固液相変化による低濃度 CO_2 の高効率吸収システムを報告した[3]．1 分子のジアミンが等量の CO_2 を吸収すると，カルバミン酸が固体として析出する．生成系の濃度が保たれることで平衡制約を回避し，低濃度 CO_2 の高効率吸収が可能となる．本研究では，CO_2 の化学的輸送を志向し，種々のジアミンの CO_2 吸収能を評価した．その結果，あるジアミンの DMSO 溶液が，2 等量の CO_2 をジカルバミン酸として吸収することを見出した．このうち 1 等量は室温で放出され，60℃ですべての CO_2 が放出された．これらの結果は，本システムが従来の高圧輸送システムと比べ安全な CO_2 の化学的輸送になる可能性を示している．

1) F. Neele *et al.*, *Energy Procedia,* ***2017***, 114, 6824.
2) 田中ら，*マリンエンジニアリング*, **2023**, 58, 29.
3) S. Kikkawa *et al.*, *ACS Environ. Au*, **2022**, 2, 4, 354.

プルシアンブルー類似体を用いた水蒸気を含むガスおよび水中からのメタノール吸着

（産総研）○首藤 雄大・川本 徹・髙橋 顕

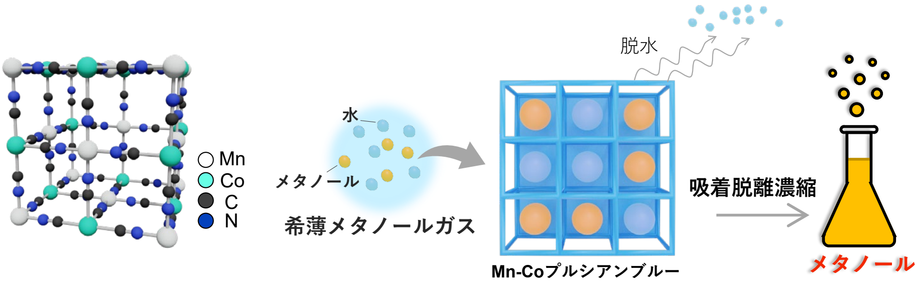
The Purification of Methanol using Prussian blue analogues capturing trace methanol gas

(National Institute of Advanced Industrial Science and Technology) ○Yuta Shudo, Tohru Kawamoto, Akira Takahashi

Conventional methanol recovery processes are highly energy-intensive; processes using selective adsorbents that consume low energy are preferable. However, conventional adsorbents have low methanol selectivity under humid conditions. This study develops a selective methanol adsorbent, manganese hexacyanocobaltate (MnHCC), a Prussian blue analogue, that enables the efficient removal and reuse of methanol. MnHCC adsorbs 4.8 mmol-methanol/g-adsorbent at 25 degrees in a humid gas containing 5000 ppmv of methanol, which is five times higher than the adsorption capacity of activated carbon (0.86 mmol/g). Although MnHCC exhibits the simultaneous adsorption of methanol and water, it has a higher adsorption enthalpy for methanol than that for water. Thus, pure methanol (95%) was recovered via thermal desorption after dehydration.

Keywords：Adsorption; Methanol; Prussian blue; Porous materials.

本研究では水蒸気を含むガスからメタノールを選択的に濃縮できる吸着材を開発した。排ガス中のメタノールは大気放出される前にエネルギーを余分に加えて燃焼無害化処理している。そこで本研究ではメタノールを選択的に脱離させる Mn-Co プルシアンブルー類似体を開発することで希薄なメタノールガスから 95wt%の高濃度なメタノール液を回収することに成功した。このプロセスに必要なエネルギーを計算したところ、既存のメタノール製造プロセスよりも低いエネルギーでメタノールを資源化できることが明らかとなった。また最近では水中のメタノールを吸着できる Mn-Fe プルシアンブルー類似体を開発した。Mn-Fe プルシアンブルー類似体は 1000mg-MeOH/L のメタノール水から 0.36mg-MeOH/L 吸着することができ、こちらも活性炭と比較して 3 倍程度高い吸着量を示した。



図：Mn-Co プルシアンブルーの構造とメタノール濃縮プロセス

1) Recovery of Pure Methanol from Humid Gas Using Mn–Co Prussian Blue Analogue. Y. Shudo, S. Numano, T. Kawamoto, and A. Takahashi*, *ACS Appl. Mater. Interfaces,* **2023**, *15*, 11977–11982.

作業環境測定での活性炭・シリカゲル捕集剤と有機溶剤抽出効率

（独立行政法人労働者健康安全機構 労働安全衛生総合研究所）○安彦 泰進

Dependence of Extraction Efficiency of Activated Carbon and Silica Gel Sampling Agents for Work Environment Measurement on the Concentration of Organic Solvents（*Work Environment Research Group*, *National Institute of Occupational Safety and Health*, *Japan Organization of Occupational Health and Safety*）○Hironobu Abiko

Activated carbon and silica gel are commonly used as sampling agents of organic solvent vapor in work environment measurement established by the Industrial Safety and Health Act in Japan. In the measurement, extraction efficiency of organic solvent from the agents is particularly important for accuracy of determination especially in the low concentration region of the vapor. In this study, we have measured the efficiencies of the agents using several types of organic solvent to investigate their concentration dependence. Clarification of the concentration dependence is necessary in examining of effective measurement methods using the agents in combination.

Keywords : *Activated Carbon*; *Extraction Efficiency*; *Organic Solvent Vapor*; *Silica Gel*; *Work Environment Measurement*

労働安全衛生法に基づく作業環境中の有機溶剤蒸気（有機ガス）濃度の測定方法には、活性炭などの捕集剤が充填された捕集管と吸引ポンプにより一定時間の濃縮捕集を行った後、各種の有機溶媒で対象の有機溶剤成分を捕集剤から抽出して測定を行う固体捕集法がある1-3)。上記の濃度測定においては、近年は従来よりもさらに低濃度の領域の精確な測定にも関心が持たれているが、現在の主要な捕集剤である活性炭は有機溶剤の種類や濃度によっては抽出効率（脱着率）が好ましくなく、測定精度に影響を生じることが指摘されている。一方、シリカゲルは疎水性の活性炭を補う捕集剤とされるが、双方の適切な使い分けの詳細は未だ不明である。そこで本研究は双方での各種有機溶剤の脱着率の比較を進め、これらの併用による効果的な測定方法の検討を目的とする。当日の発表では、固体捕集法や各捕集剤の概要について示すと共に、幾つかの有機溶剤について活性炭捕集剤とシリカゲル捕集剤での抽出効率の濃度依存性を比較した結果（Fig.1）からの考察を報告する。

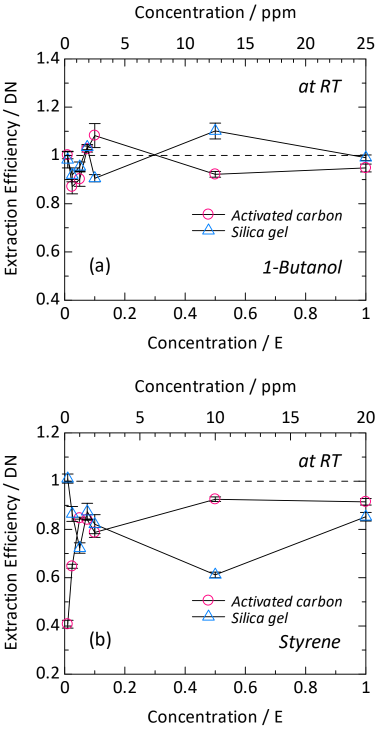


Fig.1 Examples of comparison of extraction efficiencies of organic solvent components determined by the direct addition method 3) between the petroleum-based activated carbon specimen (40 mg) and the silica gel specimen (70 mg). E= the control concentration as defined by the Industrial Safety and Health Act in Japan. DN= dimensionless number. RT= room temperature.

【参考文献】

1）公益社団法人日本作業環境測定協会編．作業環境測定ガイドブック 5［有機溶剤（特別有機溶剤を含む)］— 物質別各論 初版（2019）.

2）安彦泰進．産業衛生学雑誌 **62** (2020) 192−197.

3）H. Abiko. *SN Applied Sciences* **3** (2021) Article number 206.

ヘテロジトピックレセプターを用いた塩化リチウムの選択的固-液抽出

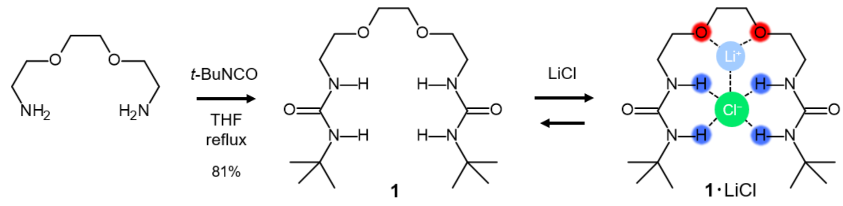
(山形大理[1]・レゾナック[2]) ○三室 翼[1]・平澤 学[1,2]・近藤 慎一[1]
Selective Solid-Liquid Extraction of Lithium Chloride with Heteroditopic Receptors ([1]*Faculty of Science, Yamagata University*, [2]*Resonac Corporation*) ○ Tsubasa Mimuro,[1] Manabu Hirasawa,[1,2] Shin-ichi Kondo[1]

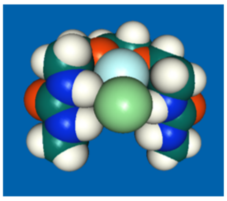
As the demand for lithium has increased over the years,1) extraction from seawater and used batteries has attracted attention. In addition, heteroditopic receptors are expected to be effective in the extraction of certain salts.2) However, there are still no reported examples of practical use of the receptor due to the inadequate capability. We report the development of a highly selective extraction method for lithium chloride by solid-liquid extraction at high concentration by using heteroditopic receptors with high solubility. Receptor **1** recognizes a cation at the ether site and an anion at the urea site, and the cavity size was found to be well match with LiCl. Solid-liquid extraction with **1** showed more than 70% recovery of LiCl even when K^+ and Na^+ were present 10 and 100 times higher, respectively. Li salt was also recovered from Uyuni lake salt and bitterness. The new recovery method also allows the use of industrial organic solvents and the reuse of receptors, and we have developed a more practical method for the recovery of LiCl.

Keywords : solid-liquid extraction, molecular recognition chemistry, host-guest chemistry, lithium salt

近年、リチウムの需要が逼迫する中、より効果的な生産法をもとめ、海水や廃電池からの抽出が注目されている1)。また、イオン対認識が可能なヘテロジトピックレセプターは、特定の塩の抽出が期待されている2)。しかし、レセプターの選択性や抽出能が十分でないため、実用的な報告例は未だ存在しない。本研究では、合成が簡便で溶解度の高いヘテロジトピックレセプターを用いることで、高濃度な固液抽出による塩化リチウムの高選択的な抽出手法を開発したことを報告する。

ヘテロジトピックなレセプター**1** は、エーテル部位でカチオンを、尿素部位でアニオンを認識し、分子の形成する空隙のサイズから、LiCl への選択性が高いことが分かっている。実際の固液抽出では、K^+が 10 倍、Na^+が 100 倍競合する条件においても LiCl の回収率が 7 割以上を示し、天然のサンプルであるウユニ塩湖の塩や日本近海で得られた苦汁などからも Li 塩を回収することができた。また、新たな回収手法は、工業的な有機溶媒の使用やレセプターの再利用が可能であり、より実用的な LiCl の回収手法を開発した。




B3LYP/6-31+G(d) in MeCN (PCM)

1) S. Mohr, G. Mudd, D. Giurco, *Minerals*, **2012**, *2*, 65.
2) J. Mahoney, A. Beatty, B. Smith, *Inorg. Chem.*, **2004**, *43*, 7617.