

Indium extraction with HDEHP in menthol-based deep eutectic solvent

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The study of indium extraction by using liquid phase chemistry techniques has been ongoing in the Heavy Elements, Nuclear and Radiochemistry Group at the Cyclotron Institute of Texas A&M University. This study aims to contribute to the fundamental research on the chemistry of the superheavy elements, specifically element 113 (E113). E113 is the newest member of group 13 of the Periodic Table of Elements and its chemical properties have not yet been studied extensively. Based on theoretical predictions, this element is expected to be volatile [1]. A gas-phase chemistry experiment of E113 was conducted at the Joint Institute for Nuclear Research (JINR) in Dubna, Russia in an attempt to reveal its chemical properties. Although the result of that experiment was somewhat inconclusive, it was concluded that E113 is highly volatile and thus confirmed the theoretical predictions [2]. More experiments are required in order to provide more information about the chemical properties of E113. The study of homologs (other elements in the same group) is commonly employed to provide such information. Indium is the lighter homolog of E113, and our group has previously studied indium behavior in hydrochloric acid solutions by means of ion exchange and liquid-liquid extraction techniques [3]. In the current work, the performance of the liquid-liquid extraction (LLE) technique for indium extraction is developed and explored further. The description of experimental procedure and preliminary results are presented in the following paragraphs.

The LLE system in this work uses a deep eutectic solvent (DES) as the organic phase to substitute for conventional organic compounds. DESs are characterized by lower melting points compared to their individual constituents. They are prepared by mixing two components that act as hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD), from which hydrogen bonds form and facilitate liquefaction of the final mixture [4]. DESs are generally believed to be biodegradable, thus they pose less hazard to environment compared to conventional solvents [5]. In this work, a DES comprised of DL-menthol and lauric acid was synthesized in our laboratory. DL-menthol and lauric acid which were originally solid at room temperature were mixed with molar ratio 2:1. The mixture was heated in a water bath at 90°C until it formed a homogenous liquid phase. Subsequently, the solution was cooled down to room temperature, shaken for 5 minutes with a Vortex mixer at 3000 rpm, and centrifuged for 1 minute at 4400 rpm before usage.

Indium stock solution was prepared by adding an appropriate amount of radioisotope indium-111 (half-life 67.32 hours) in 0.2 M hydrochloric acid (HCl). The aqueous phase consists of 10 µL indium from the stock solution and 490 µL of HCl of various concentrations. Equal volumes of aqueous and organic phases (500 µL) were placed in a 5 mL polyethylene tube, shaken with a Vortex mixer for 5 minutes at 3000 rpm, and then centrifuged for 1 minute at 4400 rpm. After the centrifugation, 250 µL was drawn from each phase and subsequently assayed with a sodium iodide detector according to a technique described elsewhere [6]. The distribution of indium between the two phases (D) was calculated by taking the ratio of the activity in the organic phase to the activity in the aqueous phase. The result showed that

indium was poorly extracted ($D \leq 1$ in pH 1 – 6). In order to increase the extraction yield, a complexing agent was added into the organic phase as the extractant of indium.

In this work, an organophosphorus acidic extractant, namely di-(2-ethylhexyl)-phosphoric acid (HDEHP), was used as the complexing agent for indium. The structure of HDEHP is presented in Fig. 1.

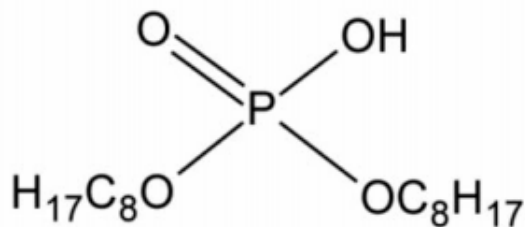


FIG. 1. Structure of HDEHP.

The organic phase for indium extraction with this system consists of 30% (v/v) HDEHP in DES menthol-lauric acid, and the extraction was done from HCl media. The effect of pH on indium extraction was investigated and the result is presented in Fig. 2. As can be seen from the figure, indium was extracted at $\text{pH} > 0.6$ and $\text{pH} < 2.8$ ($D \geq 10$). Generally, the distribution ratios of indium extraction increase with increasing pH up to pH 2, and they decrease above this pH.

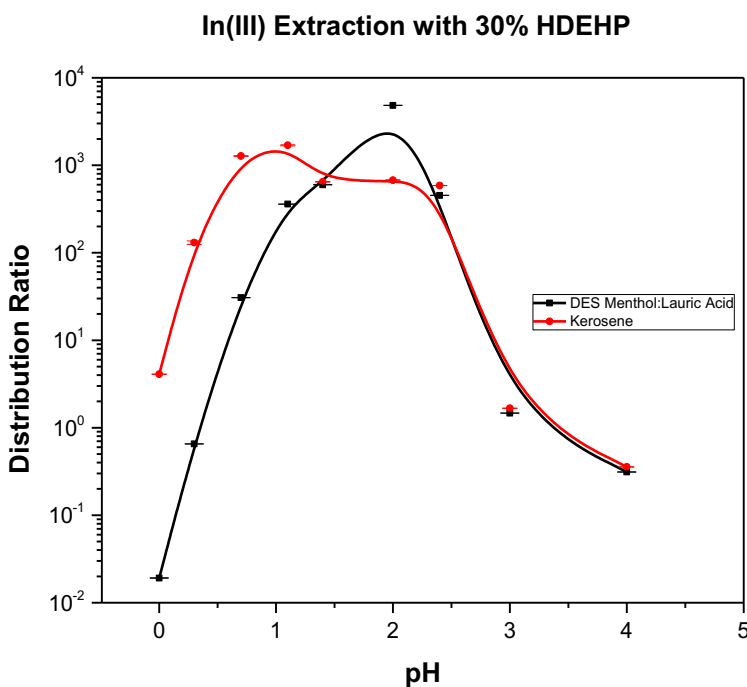


FIG. 2. Extraction of indium with HDEHP in DES menthol-lauric acid and kerosene. The lines are drawn to guide the eye.

Addition of HDEHP results in a significant increase in extraction yield. This leads to the conclusion that HDEHP is responsible for the extraction of indium from the aqueous phase to the organic phase. To check the effectiveness of DES menthol-lauric acid as the organic solvent, the extraction of indium into HDEHP with the DES menthol-lauric acid was compared with extraction into HDEHP with kerosene, a conventional organic solvent which is commonly used in LLE. In both systems, 30% (v/v) HDEHP was added to the organic phase. Based on the results in Fig. 2, the distribution ratios of indium extraction into HDEHP with kerosene are generally higher at pH below 1.1. As the pH increases, the extraction yield with kerosene decreases and reaches a plateau at pH 1.4 – 2.4. Beyond this pH range, the distribution ratios decrease with a similar trend as extraction with DES menthol-lauric acid. Based on these results, best extraction with kerosene and HDEHP was obtained at pH 1.1. Experiments are still ongoing to confirm this result. However, this preliminary result is a good indication that DES menthol-lauric acid can be a proper candidate to replace toxic and flammable organic solvents in LLE of metals.

- [1] A. Türlér and V. Pershina, *Chem. Rev.* **113**, 1237 (2013).
- [2] S.N. Dmitriev, N.V. Aksenov, Y.V. Albin, G.A. Bozhikov, M.L. Chelnokov, V.I. Chepygin, R. Eichler, A.V. Isaev, D. E. Katrasev, V.Y. Lebedev, O.N. Malyshev, O.V. Petrushkin, L.S. Porobanuk, M.A. Ryabinin, A.V. Sabel’Nikov, E.A. Sokol, A.V. Svirikhin, G.Y. Starodub, I. Usoltsev, G.K. Vostokin, and A.V. Yeremin, *Mendeleev Commun.* **24**, 253 (2014).
- [3] E.E. Tereshatov, M.Yu Boeltova, and C.M. Folden III, *Solvent Extr. Ion Exch.* **33**, 607 (2015).
- [4] F. Pena-Pereira and J. Namieśnik, *ChemSusChem.* **7**, 1784 (2014).
- [5] B.D. Ribeiro, C. Florindo, L.C. Iff, M.A.Z. Coelho, and I.M. Marrucho, *ACS Sustainable Chem. Eng.* **3**, 2469 (2015).
- [6] E.E. Tereshatov and C.M. Folden, *Progress in Research*, Cyclotron Institute, Texas A&M University (2014-2015), p. IV-66; [http://cyclotron.tamu.edu/2015 progress report/4 superconducting cyclotron and instrumentation/iv_66-74_a labview solution.pdf](http://cyclotron.tamu.edu/2015%20progress%20report/4%20superconducting%20cyclotron%20and%20instrumentation/iv_66-74_a_labview_solution.pdf) (accessed May 20, 2016).
- [7] M. Regel-Rosocka, F.J. Alguacil, *REVMETAL Revista de Metalurgia.* **49**, 292 (2013).