Separation of GaCl$_3$ from AlCl$_3$ by Solid-Liquid Extraction and Stripping using Anhydrous $n$-Dodecane and NaCl

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Supporting information
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EXPERIMENTAL DETAILS

Materials

$n$-Dodecane (anhydrous, 99%), $n$-hexane (anhydrous, 99%), GaCl$_3$ (ultra-dry, 99.999%), LiCl (analytical reagent) and KCl (analytical reagent) were purchased from Alfa Aesar; NaCl (analytical reagent), ethanol (99%) and acetone (99%) were obtained from Fisher Chemical; InCl$_3$ (99.995%) and AlCl$_3$ (extra pure anhydrous, 99%) were purchased from Acros Organics; SbCl$_3$ (99.0%) and Triton X-100 were purchased from Sigma–Aldrich; silicone solution in isopropanol was purchased from SERVA Electrophoresis GmbH; standard solutions of Ga, In, Sb, La, Al, Li, Na and K (1000 µg·mL$^{-1}$ in 3–5% nitric acid) were purchased from Chem-Lab.

Experimental procedures

**Extraction rate.** To investigate the influence of mixing times on separation efficiency, extraction and back-extraction rates were evaluated. For the extraction rate, a series of 50 mL round-bottom flasks with 0.50 g of GaCl$_3$, 0.20 g of InCl$_3$ and 10 mL of anhydrous $n$-dodecane were shaken for 1, 2, 5, 10, 15, 20 and 30 min, respectively. The corresponding $n$-dodecane solution of each sample was stripped by water and the resultant aqueous solution was measured by TXRF. For the back-extraction rate, a series of 50 mL round flasks with 10 mL of the loaded $n$-dodecane containing 50 g·L$^{-1}$ GaCl$_3$ was back-extracted by NaCl (NaCl/GaCl$_3$ ratio was 10) and shaken for 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 and 5.0 h, respectively. $n$-Dodecane in each of the flask after back-extraction was stripped by water and the resultant aqueous solution was measured by TXRF.

**Mass balance of the process.** 0.505±0.005 g GaCl$_3$ (0.200±0.002 g Ga), 1.14 g AlCl$_3$ (molar ratio of AlCl$_3$:GaCl$_3$ = 3) and 10 mL of anhydrous $n$-dodecane in a 50 mL was shaken for 30 min, followed by settling for 5 min. The loaded anhydrous $n$-dodecane was then removed by a syringe and added to another round-bottom flask with 1.66 g NaCl (molar ratio of NaCl:GaCl$_3$ = 10, assuming that the 0.5 g GaCl$_3$ in the GaCl$_3$/AlCl$_3$ mixture was completely extracted). The AlCl$_3$ residue (containing about 0.2 mL $n$-dodecane due to incomplete solid-liquid separation by syringe) after extraction of GaCl$_3$ was dissolved in water and measured for Ga by ICP-OES (Perkin Elmer Optima 83000). The amount of detected Ga was marked as $M_1$. The flask with loaded anhydrous $n$-dodecane and NaCl was shaken for 120 min, followed by settling for 5 min. The anhydrous $n$-dodecane after
stripping by NaCl was subsequently removed and then stripped by water, and the resultant aqueous solution was measured by ICP-OES. The amount of detected Ga was marked as M2. The NaCl residue after stripping GaCl3 (containing about 1.5 mL n-dodecane due to incomplete solid-liquid separation by syringe) was also dissolved in water and the resultant aqueous solution was measured by ICP-OES. The amount of detected Ga was marked as M3. The test was conducted in triplicate. M1, M2 and M3 was used to evaluate mass balance of the whole process.

It is essential that the separation process is carried out in strictly anhydrous conditions (e.g. using a glovebox) and that anhydrous solvents are used, because GaCl3 is highly moisture sensitive. Manipulation of GaCl3 on an open bench or failing to use carefully dried solvents will result in hydrolysis of GaCl3. The hydrolysis products are not soluble in hydrocarbon solvents, in contrast to anhydrous GaCl3 itself.

RESULTS AND DISCUSSIONS

Extraction of GaCl3 by n-hexane. The extraction of GaCl3 from binary mixtures of GaCl3/SbCl3, GaCl3/InCl3 and GaCl3/AlCl3 using anhydrous n-hexane as solvent, in addition to n-dodecane, were conducted and Raman spectra were recorded for the solid residues after extraction (Fig. S1). The Raman bands at 127, 206, 354 and 379 cm\(^{-1}\) for the mixture of GaCl3/SbCl3 using n-hexane as solvent (Fig. S1-a) are almost the same as the bands observed when n-dodecane was used as solvent (Fig. 2-a). In terms of the binary mixture of GaCl3/InCl3, Fig. S1-b displays a small extra band at 394 cm\(^{-1}\) compared to Fig 2-b, which can be assigned to the species of [GaCl4]\(^{-}\) (reported at 394 cm\(^{-1}\)). The Raman spectra of the GaCl3/AlCl3 mixture and pure AlCl3 are almost the same (Fig. S1-c), meaning that no [AlCl2][GaCl4] or [GaCl2][AlCl4] was formed.

Stripping mechanism. To validate the mechanism of stripping, Raman spectra of pure MCl (M=Li, Na and K) and the solid residues after stripping GaCl3 by MCl were recorded and presented in Fig. S3. The spectra of the pure MCl salts did not show characteristic peaks due to the weak vibrations of these salts. However, when they interact with dissolved GaCl3, their spectra become visible and valuable information can be obtained. For the stripping with LiCl, a peak can be seen at 347 cm\(^{-1}\), which is assigned as one of the main [GaCl4]\(^{-}\) vibrations, reported at 346 cm\(^{-1}\). For the stripping with NaCl, peaks can be seen at 347, 362, 371 and 379 cm\(^{-1}\), corresponding to reported vibrations at 346, 359, 373 and 380 cm\(^{-1}\), respectively, for [GaCl4]\(^{-}\). Similar vibrations can be
observed for the back-extraction with KCl, at 353 and 374 cm\(^{-1}\).\(^1\)\(^-\)\(^4\) Besides these vibrations, some other peaks can be observed at lower wavenumbers. However, spectral interpretation of these peaks is difficult due to the presence of a spurious double peak in the 150–170 cm\(^{-1}\) region.\(^5\) Therefore formation of the ionic compounds of LiGaCl\(_4\), NaGaCl\(_4\) and KGaCl\(_4\) can be concluded for stripping. Besides, the formation of KGa\(_2\)Cl\(_7\) and KGa\(_3\)Cl\(_{10}\) is also possible because these species have been observed.\(^6\)\(^,\)\(^7\)

**Extraction and stripping rate.** The rates of GaCl\(_3\) extraction by anhydrous \(n\)-dodecane and the stripping from loaded \(n\)-dodecane by NaCl are presented in Fig. S4. The equilibrium of extraction can be reached in 1 min, while the stripping takes up to 4 h to complete.

**Mass balance of the process.** \(M_1\), \(M_2\) and \(M_3\) was found to be 0.02±0.003 g, 0.023±0.01 g and 0.161±0.01 g, respectively. The sum of them is 0.205±0.007 g, close to the initial amount of 0.200±0.002 g, indicating a good overall mass balance. Based on the overall mass balance, the extraction percentage of GaCl\(_3\) from the GaCl\(_3\)/AlCl\(_3\) mixture is about 90%, and the stripping percentage by NaCl from the loaded \(n\)-dodecane is about 88%. It is worth to note that the incomplete separation of \(n\)-dodecane from the solid AlCl\(_3\) and NaCl after extraction and stripping respectively, underestimates the extraction percentage and overestimates the stripping percentage.
Figure S1. Raman spectra of the pure chloride compounds and of the different separation residues after extraction of GaCl$_3$ from binary mixtures by anhydrous $n$-hexane.
Figure S2. Comparison of experimental and DFT calculated (unscaled) Raman spectra of Ga₂Cl₆.
Figure S3. Raman spectra of pure alkali metal chloride salts and of solid mixtures after stripping GaCl₃ by these salts (a: LiCl, b: NaCl, c: KCl).
Figure S4. Rates for extraction of GaCl$_3$ from GaCl$_3$/InCl$_3$ mixtures by anhydrous $n$-dodecane (a) and rates for stripping GaCl$_3$ from loaded $n$-dodecane by NaCl (NaCl/GaCl$_3$ ratio was 10) (b).
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