

# Separation of GaCl<sub>3</sub> from AlCl<sub>3</sub> by Solid–Liquid Extraction and Stripping Using Anhydrous *n*-Dodecane and NaCl

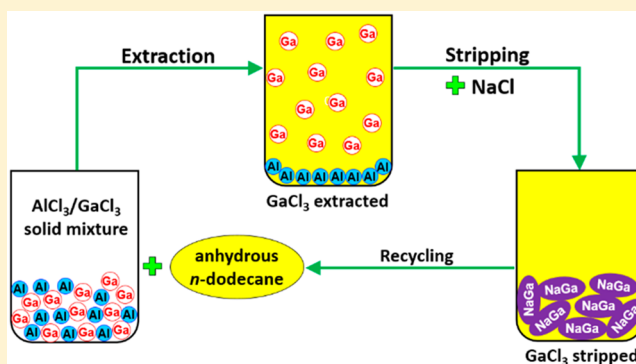
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## S Supporting Information

**ABSTRACT:** Separation of GaCl<sub>3</sub> from other associating chloride compounds (e.g. AlCl<sub>3</sub>, SbCl<sub>3</sub>, and InCl<sub>3</sub>) is generally achieved by hydrometallurgical processes. In this study, we explore the separation of GaCl<sub>3</sub> from these compounds on the basis of the exceptionally high solubility of GaCl<sub>3</sub> in hydrocarbon solvents. We found that GaCl<sub>3</sub> can be efficiently extracted by anhydrous *n*-dodecane from a solid mixture of GaCl<sub>3</sub> and AlCl<sub>3</sub>; on the contrary, SbCl<sub>3</sub> and InCl<sub>3</sub> significantly reduce the extraction of GaCl<sub>3</sub>. On the basis of Lewis acidity theory and study of the Raman spectra, it is shown that formation of the ionic compound [SbCl<sub>2</sub>][GaCl<sub>4</sub>] is responsible for the reduced GaCl<sub>3</sub> extraction. Formation of [InCl<sub>2</sub>][GaCl<sub>4</sub>] is also likely, but further study is needed to support the existence of this compound. Further making use of the strong Lewis acidity of GaCl<sub>3</sub>, GaCl<sub>3</sub> can be efficiently stripped from the loaded *n*-dodecane phase by solid NaCl through formation of NaGaCl<sub>4</sub>. The extraction of GaCl<sub>3</sub> by *n*-dodecane, in combination with its stripping by NaCl, is a solvometallurgical process that is essentially different from the hydrometallurgical processes for the separation of GaCl<sub>3</sub> and AlCl<sub>3</sub>.



## 1. INTRODUCTION

Known as “the backbone of the electronics industry”, gallium is used widely in optoelectronics and particularly for semiconductors.<sup>1–4</sup> It also finds applications in alloys<sup>5,6</sup> and biomedical applications.<sup>7</sup> Gallium does not form its own ores, but it is produced primarily as a byproduct of the treatment of bauxite for alumina production in the Bayer process.<sup>1,8</sup> Besides, secondary resources such as waste semiconductors (e.g. InGaN, GaSb) are potential sources for gallium.<sup>9–11</sup> Therefore, purification of gallium via a chloride route involves the separation of GaCl<sub>3</sub> and these associating chloride compounds, including AlCl<sub>3</sub>, InCl<sub>3</sub>, or SbCl<sub>3</sub>. Hydrometallurgical processes, such as solvent extraction and ion exchange, are the main processes for the separation of gallium from these associating elements.<sup>8,10,12–14</sup> While established, these processes usually require multiple separation stages due to the similar affinity of these compounds to extractants and ion exchangers.

In contrast to the generally negligible solubility of inorganic salts in hydrocarbons, GaCl<sub>3</sub> has the unique property of being highly soluble in aliphatic hydrocarbons: up to 1230 g of GaCl<sub>3</sub> can be dissolved in 1 L of hexane at 60 °C.<sup>15</sup> GaCl<sub>3</sub> is likely dissolved in hexane as a mixture of monomer, dimer, and even trimer, as indicated by a <sup>71</sup>Ga NMR study,<sup>16</sup> whereas GaCl<sub>3</sub> forms a  $\pi$ -complex in aromatic solvents.<sup>16,17</sup> This high solubility of GaCl<sub>3</sub> in hydrocarbons could be exploited for purification of gallium. Iwantschew and Dötzer proposed that

volatile hydrocarbons, such as *n*-pentane, *n*-hexane, and cyclohexane can be used to extract GaCl<sub>3</sub> from AlCl<sub>3</sub> and InCl<sub>3</sub>, followed by removal of the hydrocarbon solvents by distillation.<sup>15</sup> However, these solvents raise significant environmental concerns: they are volatile organic compounds (VOC) and highly flammable, and some of them, such as *n*-hexane, are neurotoxic.<sup>18–20</sup> Moreover, distillation is an energy-intensive operation. More importantly, the actual performance of GaCl<sub>3</sub> separation from other chloride compounds using hydrocarbons is not known, because no studies can be found except for the brief descriptions in the patent of Iwantschew and Dötzer. Therefore, the feasibility of GaCl<sub>3</sub> separation from other chloride compounds using hydrocarbons warrants more investigations.

In this study, we investigate the use of *n*-dodecane, which is a much less volatile and an environmentally more benign solvent, to extract GaCl<sub>3</sub>, and we explore a suitable stripping process based on precipitation rather than distillation. In addition, we discuss the extraction and stripping mechanisms. This work fits into our research program on the development of solvometallurgy.<sup>21</sup>

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## 2. EXPERIMENT AND METHODS

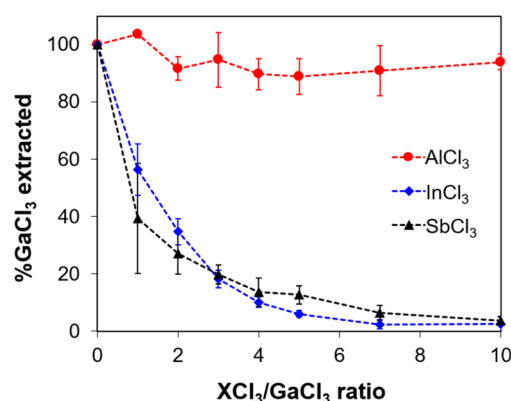
**2.1. Extraction.** Separations of GaCl<sub>3</sub> from metal chloride compounds were tested by mixing 500 mg of GaCl<sub>3</sub> with different amounts of other chloride compounds with various molar ratios of MCl<sub>3</sub>/GaCl<sub>3</sub> (M = Al, In, and Sb). Then, 10 mL of anhydrous *n*-dodecane (or *n*-hexane) was added to these mixtures and they were shaken for 30 min, although extraction equilibrium could be reached in 1 min. To analyze the extraction efficiency, the loaded *n*-dodecane phases were brought in contact with an equal volume of Milli-Q water and shaken for 60 min. The metals in the *n*-dodecane phase were found to be completely stripped, and the resultant aqueous solution was measured by total reflection X-ray fluorescence spectrometry (TXRF, Bruker S2 Picofox) or inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer Optima 8300). Raman spectra were recorded (by Bruker Vertex 70 spectrometer) for the pure compounds of AlCl<sub>3</sub>, SbCl<sub>3</sub>, and InCl<sub>3</sub> and the solid residues after extraction of GaCl<sub>3</sub> by anhydrous *n*-dodecane (or *n*-hexane) from the solid binary mixtures of GaCl<sub>3</sub>/AlCl<sub>3</sub>, GaCl<sub>3</sub>/SbCl<sub>3</sub>, and GaCl<sub>3</sub>/InCl<sub>3</sub>.

**2.2. Stripping.** LiCl, NaCl, and KCl powders were ground by a mortar grinder (Fritsch Pulverisette 2) and sieved by a sieve shaker (Fritsch Analysette 3) with a sieve mesh of 250 μm. Then the ground and sieved salts were put into a round-bottom flask and connected to a Schlenk line to dry them for 24 h at 100 °C. Subsequently, the salts were used for stripping experiments. Each of the samples containing 10 mL of loaded *n*-dodecane with 50 g·L<sup>-1</sup> GaCl<sub>3</sub> was contacted with the ground MCl (M = Li, Na, K) in varying MCl/GaCl<sub>3</sub> molar ratios and shaken for 120 min, followed by settling for 5 min. The resultant *n*-dodecane solution was then stripped by Milli-Q water by shaking for 60 min, and the aqueous solution was measured by TXRF for Ga concentration. Raman spectra were recorded for the pure salts of LiCl, NaCl, and KCl and the solid mixtures after stripping of GaCl<sub>3</sub> by these salts.

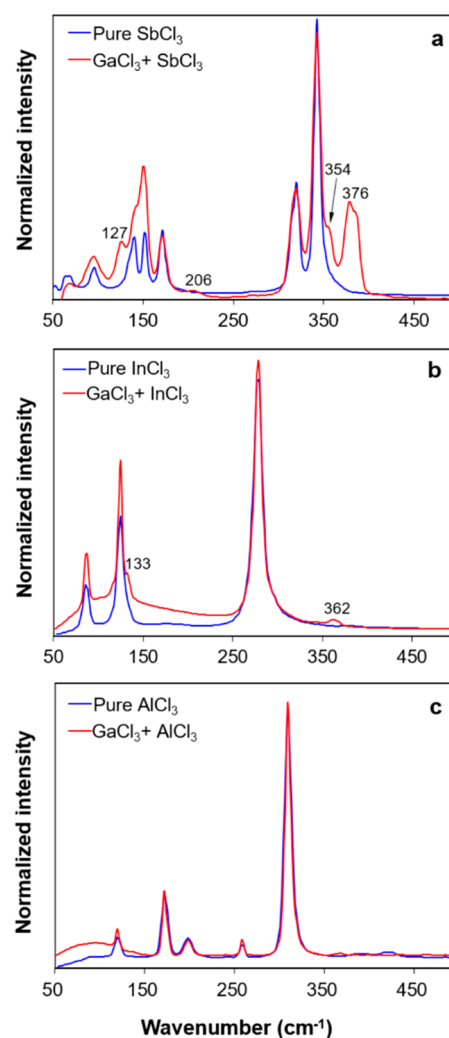
**2.3. Computational Details.** The geometries for the compounds of Ga<sub>2</sub>Cl<sub>6</sub>, InGaCl<sub>6</sub>, [GaCl<sub>4</sub>]<sup>-</sup>, and [InCl<sub>2</sub>]<sup>+</sup> were studied in the gas phase by density functional theory (DFT).<sup>22</sup> The structures were optimized at the B3LYP/def2tzvp theory of level.<sup>23–25</sup> The frequency calculations were also performed to confirm that the obtained structures correspond to minima on their potential energy surfaces (PES). Based on the optimized structures, the Raman spectra of the compounds were calculated to compare with the experimental results. All calculations were performed by Gaussian 09.<sup>26</sup> The Multiwfn code was used for data postprocessing.<sup>27</sup>

## 3. RESULTS AND DISCUSSION

**3.1. Extraction of GaCl<sub>3</sub>.** Results of GaCl<sub>3</sub> extraction by anhydrous *n*-dodecane from the solid binary mixtures of GaCl<sub>3</sub>/AlCl<sub>3</sub>, GaCl<sub>3</sub>/SbCl<sub>3</sub>, and GaCl<sub>3</sub>/InCl<sub>3</sub> are presented in Figure 1. GaCl<sub>3</sub> was efficiently extracted from GaCl<sub>3</sub>/AlCl<sub>3</sub> mixtures, even at very high AlCl<sub>3</sub>-to-GaCl<sub>3</sub> ratios. However, the presence of InCl<sub>3</sub> and SbCl<sub>3</sub> significantly reduced the extraction efficiency of GaCl<sub>3</sub>. The difference in the GaCl<sub>3</sub> extraction efficiency from the tested chloride compounds might be attributed to the differences in Lewis acidity of these compounds. The sequence of Lewis acidity is AlCl<sub>3</sub> > GaCl<sub>3</sub> > InCl<sub>3</sub> > SbCl<sub>3</sub>.<sup>28–30</sup> The GaCl<sub>3</sub> dissolved in the anhydrous *n*-dodecane may react with InCl<sub>3</sub> or SbCl<sub>3</sub>, which are weaker Lewis acids than GaCl<sub>3</sub>, forming the ionic compounds of

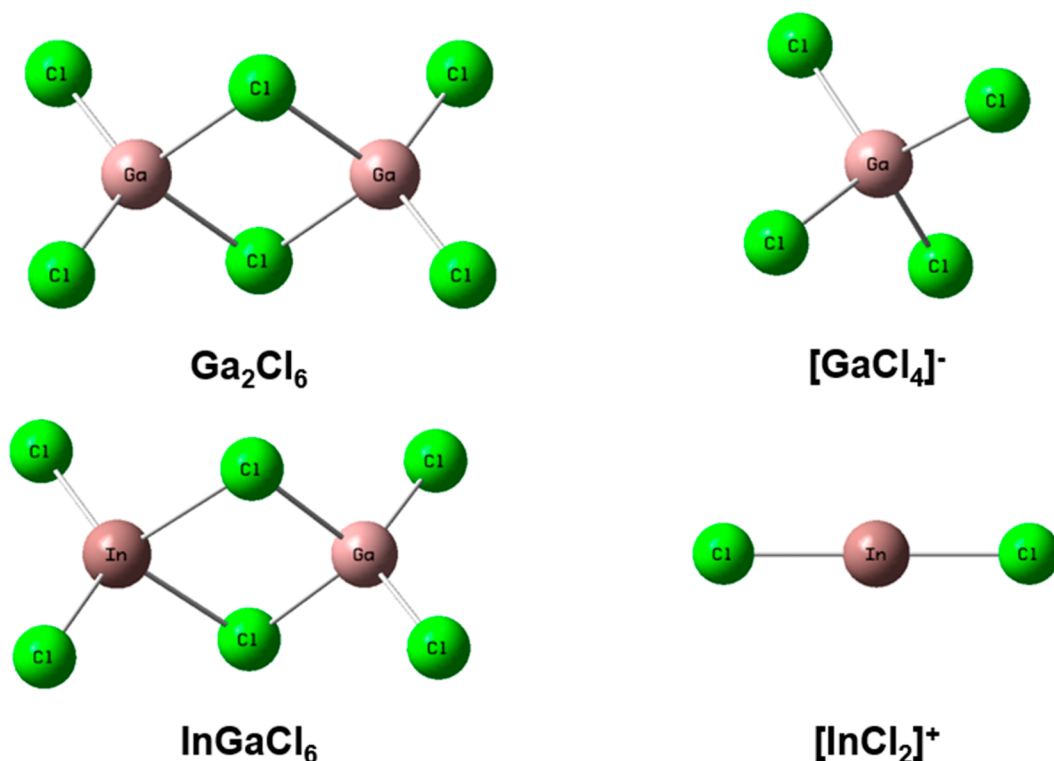


**Figure 1.** Solid–liquid extraction of GaCl<sub>3</sub> from binary mixtures of GaCl<sub>3</sub> and metal chloride compounds by anhydrous *n*-dodecane.



**Figure 2.** Raman spectra of the pure chloride compounds and of the different separation residues after solid–liquid extraction of GaCl<sub>3</sub> by anhydrous *n*-dodecane.

[InCl<sub>2</sub>][GaCl<sub>4</sub>] and [SbCl<sub>2</sub>][GaCl<sub>4</sub>] by chloride ion transfer.<sup>31</sup> These ionic compounds are insoluble in nonpolar solvents such as *n*-dodecane due to their high lattice energy and the poorly solvating properties of these solvents, thus inhibiting the extraction of GaCl<sub>3</sub> by *n*-dodecane. In contrast, as AlCl<sub>3</sub> is a stronger Lewis acid than GaCl<sub>3</sub>, one expects that the chloride



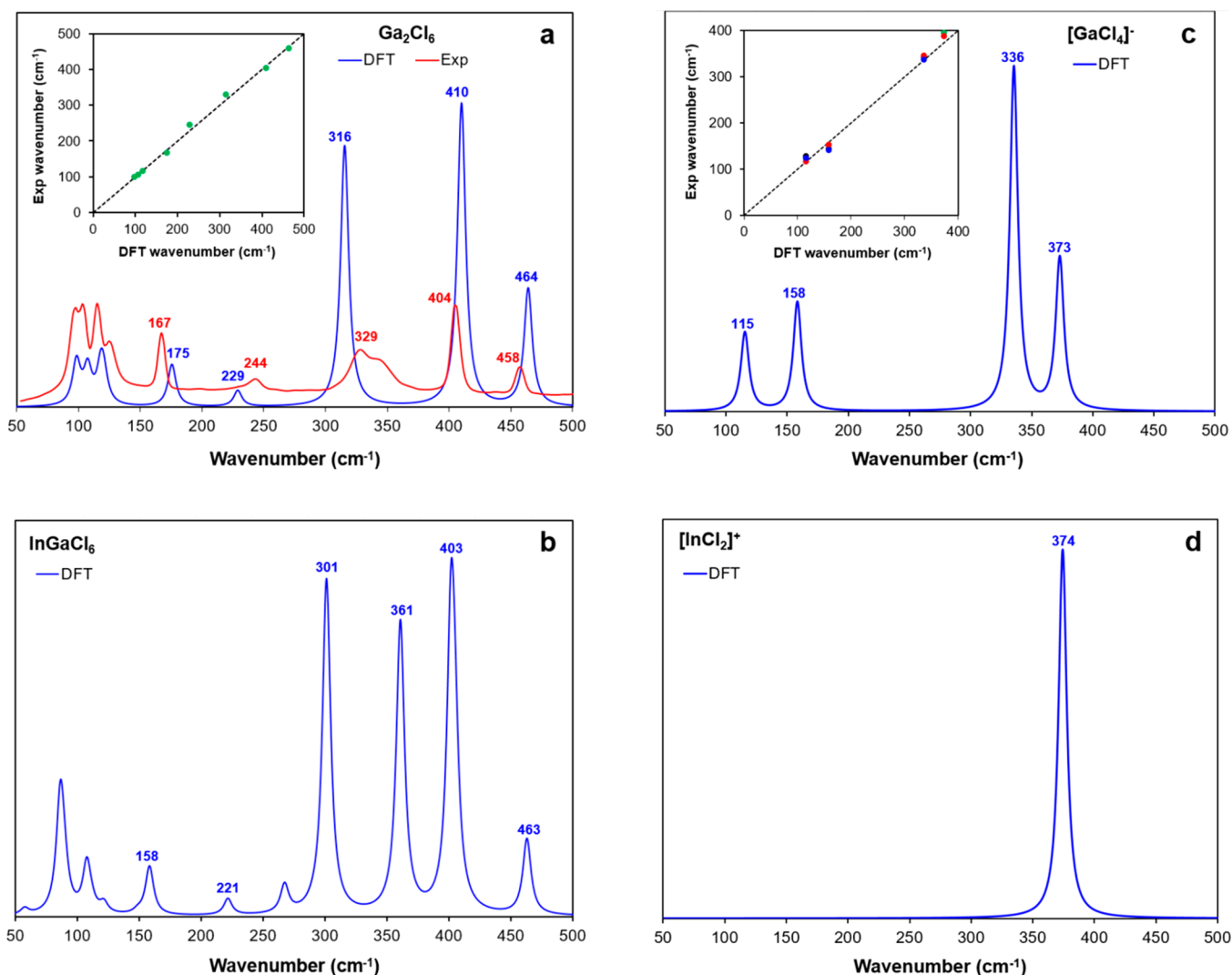
**Figure 3.** DFT optimized structures of the compounds  $\text{Ga}_2\text{Cl}_6$ ,  $\text{InGaCl}_6$ ,  $[\text{GaCl}_4]^-$ , and  $[\text{InCl}_2]^+$ .

ion transfers from  $\text{GaCl}_3$  to  $\text{AlCl}_3$ , leading to the Lewis adduct of  $[\text{GaCl}_2][\text{AlCl}_4]$ . However, the efficient extraction of  $\text{GaCl}_3$  from the  $\text{GaCl}_3/\text{AlCl}_3$  mixture indicates that the influence of  $\text{AlCl}_3$  on  $\text{GaCl}_3$  extraction is almost negligible.

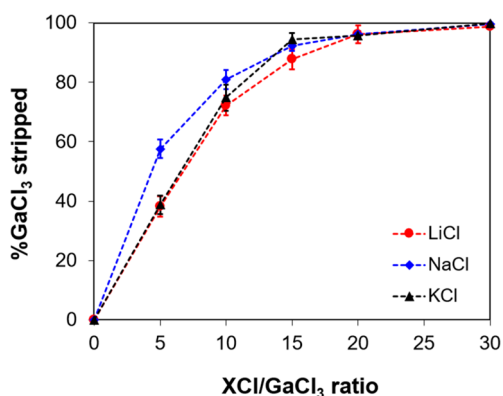
To understand how the chloride compounds affect  $\text{GaCl}_3$  extraction, Raman spectra were measured for the solid residues of the binary mixtures after extraction of  $\text{GaCl}_3$  by anhydrous *n*-dodecane (Figure 2). For the spectrum of the  $\text{GaCl}_3/\text{SbCl}_3$  mixture, four extra bands were observed in comparison with the spectrum of pure  $\text{SbCl}_3$ . The Raman bands at 127 and 354  $\text{cm}^{-1}$  can be assigned to the  $[\text{GaCl}_4]^-$  species, and the Raman bands at 206 and 376  $\text{cm}^{-1}$  can be assigned to  $[\text{SbCl}_2]^+$ .<sup>32,33</sup> Similarly, for the Raman spectrum of the  $\text{GaCl}_3/\text{InCl}_3$  mixture, the bands at 133  $\text{cm}^{-1}$  can be assigned to  $[\text{GaCl}_4]^-$ , which is reported to be at 128  $\text{cm}^{-1}$ .<sup>33</sup> The band at 362  $\text{cm}^{-1}$  may be due to the vibration of  $[\text{InCl}_2]^+$ , as reported to be at 367  $\text{cm}^{-1}$ .<sup>34</sup> The Raman spectrum assignments indicate the formation of the ionic compounds of  $[\text{SbCl}_2][\text{GaCl}_4]$  and  $[\text{InCl}_2][\text{GaCl}_4]$ . Binary  $\text{GaCl}_3/\text{InCl}_3$  mixtures have been reported to form an eutectic system,<sup>35,36</sup> but this does not exclude the possibility of forming an ionic compound under a different condition. For example, the mixed dimer  $\text{InGaCl}_6$  can be formed in the vapor phase.<sup>37</sup>  $\text{GaCl}_3$  dissolved in *n*-dodecane should have a higher propensity to react with  $\text{SbCl}_3$  or  $\text{InCl}_3$  than in the solid or molten state where the eutectic is formed. In contrast to the mixtures of  $\text{GaCl}_3/\text{SbCl}_3$  and  $\text{GaCl}_3/\text{InCl}_3$  that showed extra Raman bands, the Raman spectrum of a  $\text{GaCl}_3/\text{AlCl}_3$  mixture was almost identical to that of pure  $\text{AlCl}_3$ , indicating that the formation of either  $[\text{AlCl}_2][\text{GaCl}_4]$  or  $[\text{GaCl}_2][\text{AlCl}_4]$  is unlikely. The absence of formation of an ionic compound for the  $\text{GaCl}_3/\text{AlCl}_3$  mixture can be explained by the very similar Lewis acidity of  $\text{GaCl}_3$  and  $\text{AlCl}_3$ ,<sup>28–30</sup> and this result is consistent with the efficient solid–liquid extraction of  $\text{GaCl}_3$  from the binary mixture of  $\text{GaCl}_3/\text{AlCl}_3$

(Figure 1).  $\text{GaCl}_3$  and  $\text{AlCl}_3$  also form eutectic mixtures,<sup>36,38</sup> but  $\text{AlCl}_3$  does not affect the extraction of  $\text{GaCl}_3$ , indicating that the eutectic does not suppress  $\text{GaCl}_3$  extraction. Similarly, formation of a simple eutectic between  $\text{GaCl}_3$  and  $\text{InCl}_3$  cannot explain the reduced  $\text{GaCl}_3$  extraction, and formation of an ionic compound might be a more reasonable explanation. To validate the Lewis adduct formation, the same extraction experiments were conducted using anhydrous *n*-hexane, and similar Raman spectra were observed for the extraction residues (Figure S1).

Because the ionic compound  $[\text{InCl}_2][\text{GaCl}_4]$  has not been reported yet, more studies are required to confirm the formation of this species. Besides the formation of the ionic compound  $[\text{InCl}_2][\text{GaCl}_4]$ , the mixed dimer  $\text{InGaCl}_6$  may be formed in the mixture of  $\text{InCl}_3$  and  $\text{GaCl}_3$ , which has been reported in the vapor phase of the  $\text{InCl}_3\text{--GaCl}_3$  system by Buraya et al.<sup>37</sup> We optimized structures of the relevant compounds in this study by DFT calculations (Figure 3) and generated their Raman spectra, which are used to discuss the two possible compounds. Pure  $\text{GaCl}_3$  is a dimer ( $\text{Ga}_2\text{Cl}_6$ ),<sup>39</sup> and its Raman spectrum has been reported by various researchers.<sup>40,41</sup> There is a good match between the calculated Raman spectrum of  $\text{Ga}_2\text{Cl}_6$  and the corresponding experimental spectrum (Figure S2), although the shifts for the bands at 244 and 329  $\text{cm}^{-1}$  are relatively large. The good match indicates that the DFT method used in this study is suitable for calculating this compound. The computed spectrum has an overall red shift, which is consistent with the observation of Timoshkin et al.,<sup>42</sup> who found that at the B3LYP level of theory, the low frequency vibrations ( $<500 \text{ cm}^{-1}$ ) are underestimated and the high frequency vibrations are overestimated by DFT computation. Despite the fact that there are available coefficients for scaling the frequency of this level of theory (e.g., coefficients given by Bao et al.<sup>43</sup>), these



**Figure 4.** Raman spectra: (a) experimental and DFT calculated spectra of  $\text{Ga}_2\text{Cl}_6$  and comparison of the two spectra; (b) DFT calculated spectrum of  $\text{InGaCl}_6$ ; (c) DFT calculated spectrum of  $[\text{GaCl}_4]^-$  and its comparison with literature data of Shamir and Rafaeloff,<sup>32,33</sup> and Gerding and Koningstein;<sup>45</sup> (d) DFT calculated spectrum of  $[\text{InCl}_2]^+$ .



**Figure 5.** Stripping of  $\text{GaCl}_3$  from the loaded *n*-dodecane solution by alkali metal chlorides.

coefficients are suitable for high frequency vibrations but not suitable for low frequency vibrations, which is the case in this study. Therefore, we followed the treatment in the study of Timoshkin et al.,<sup>42</sup> to regress scaling coefficients using the

following equation, based on the experimental spectrum of  $\text{Ga}_2\text{Cl}_6$ .

$$w_{\text{Exp}} = A \times w_{\text{DFT}} + B \quad (1)$$

where  $w_{\text{Exp}}$  and  $w_{\text{DFT}}$  are the experimental and computed wavenumber, respectively. The obtained coefficients are  $A = 0.9878$  and  $B = 14.66 \text{ cm}^{-1}$ , and the correlation coefficient is 0.996. After scaling (Figure 4a), the computed spectrum matches better with the experimental spectrum. The computed spectra of  $\text{InGaCl}_6$ ,  $[\text{GaCl}_4]^-$ , and  $[\text{InCl}_2]^+$  were also scaled using the same coefficients (Figure 4).

$\text{InGaCl}_6$  exhibits a similar structure as  $\text{Ga}_2\text{Cl}_6$  (Figure 3), and its Raman spectrum resembles that of  $\text{Ga}_2\text{Cl}_6$  except for an extra band at  $361 \text{ cm}^{-1}$  (Figure 4b), which is mainly due to the symmetric stretching of  $\text{In}-\mu^1-\text{Cl}$ . Since the Raman intensity at  $403 \text{ cm}^{-1}$  for  $\text{InGaCl}_6$ , which corresponds to the band at  $404 \text{ cm}^{-1}$  for the experimental  $\text{Ga}_2\text{Cl}_6$  spectrum, is high, a band at around  $404 \text{ cm}^{-1}$  should be observable if  $\text{InGaCl}_6$  were formed. The absence of the band in Figure 2b indicates that  $\text{InGaCl}_6$  was not formed. In addition, the structures of the mixed dimer of  $\text{InGaCl}_6$  and the dimer of  $\text{Ga}_2\text{Cl}_6$  are so similar that they are expected to have similar solubility properties; that

is,  $\text{InGaCl}_6$  should be soluble in anhydrous *n*-dodecane since  $\text{Ga}_2\text{Cl}_6$  is highly soluble in anhydrous *n*-dodecane. However,  $\text{InCl}_3$  suppressed the extraction of  $\text{GaCl}_3$ , meaning that a compound that is insoluble in anhydrous *n*-dodecane was formed.

The calculated  $[\text{GaCl}_4]^-$  exhibits a tetrahedral structure, and the Raman spectrum shows four bands at  $115\text{ cm}^{-1}$ ,  $158\text{ cm}^{-1}$ ,  $336\text{ cm}^{-1}$ , and  $373\text{ cm}^{-1}$ , corresponding to experimental observations at around  $128\text{ cm}^{-1}$ ,  $153\text{ cm}^{-1}$ ,  $346\text{ cm}^{-1}$ , and  $390\text{ cm}^{-1}$ , respectively. The calculated  $[\text{InCl}_2]^+$  exhibits a linear structure, and the Raman spectrum shows only one band at  $374\text{ cm}^{-1}$  due to the symmetric stretching of  $\text{In}-\text{Cl}$ , which matches well with the reported band at  $367\text{ cm}^{-1}$ .<sup>34</sup> Kloo and Taylor reported spectroscopic data of solid  $[\text{InCl}_2(15\text{-crown-5})][\text{InCl}_4]$  but did not report the exact structure.<sup>34</sup> In a similar study, Kloo and Taylor reported that the  $\text{I}-\text{In}-\text{I}$  angle is  $170.1^\circ$  in the solid compound of  $[\text{InI}_2(18\text{-crown-6})][\text{InI}_4]$ .<sup>44</sup> In this compound, the  $[\text{InI}_2]^+$  structure is almost linear. Besides, the coordination number of indium in this compound was estimated to be less than four based on the relatively short bond length of  $\text{In}-\text{I}$ . Considering the similarity of  $[\text{InCl}_2]^+$  and  $[\text{InI}_2]^+$ , the computed linear  $[\text{InCl}_2]^+$  is reasonable. Therefore, the bands at  $362$  and  $366\text{ cm}^{-1}$  in Figure 2b and Figure S1-b, respectively, can be assigned to  $[\text{InCl}_2]^+$ , indicating the formation of  $[\text{InCl}_2][\text{GaCl}_4]$ . Formation of the ionic compound  $[\text{InCl}_2][\text{GaCl}_4]$  also explains why the extraction of  $\text{GaCl}_3$  was suppressed by  $\text{InCl}_3$ , because ionic compounds are insoluble in hydrocarbons. In summary, formation of  $[\text{InCl}_2][\text{GaCl}_4]$  in the  $\text{InCl}_3/\text{GaCl}_3$  mixture after extraction is very likely. However, formation of  $[\text{InCl}_2][\text{GaCl}_4]$  contradicts with the formation of an eutectic between  $\text{GaCl}_3$  and  $\text{InCl}_3$ . Further studies are needed to confirm the speciation of  $\text{GaCl}_3$  and  $\text{InCl}_3$  mixtures.

**3.2. Stripping of  $\text{GaCl}_3$ .** With the knowledge that the chloride is transferred and the resulting formation of ionic complexes can inhibit the dissolution of  $\text{GaCl}_3$ , advantage of it was taken to strip  $\text{GaCl}_3$  from the loaded *n*-dodecane solutions using alkali metal chlorides.  $\text{LiCl}$ ,  $\text{NaCl}$ , and  $\text{KCl}$  that were ground and sieved with a  $250\text{ }\mu\text{m}$  sieve mesh were tested for the stripping of  $\text{GaCl}_3$  for various  $\text{MCl}/\text{GaCl}_3$  ( $\text{M} = \text{Li}, \text{Na},$  and  $\text{K}$ ) molar ratios (Figure 5). The efficiency of stripping by  $\text{LiCl}$ ,  $\text{NaCl}$ , and  $\text{KCl}$  is comparable, although  $\text{NaCl}$  is slightly more efficient when the  $\text{MCl}/\text{GaCl}_3$  ratio is less than 10. About 96% of  $\text{GaCl}_3$  can be stripped from the loaded *n*-dodecane phase when the  $\text{MCl}/\text{GaCl}_3$  is 20, and the stripping is almost complete when the ratio is 30. Raman spectra of pure  $\text{MCl}$  ( $\text{M} = \text{Li}, \text{Na},$  and  $\text{K}$ ) and the solid residues after stripping of  $\text{GaCl}_3$  by  $\text{MCl}$  were recorded, and the species of  $[\text{GaCl}_4]^-$  was clearly identified (Figure S3). It is therefore evident that the alkali chlorides interact with the dissolved  $\text{GaCl}_3$  by forming the ionic compounds of  $\text{LiGaCl}_4$ ,  $\text{NaGaCl}_4$ , and  $\text{KGaCl}_4$ , which are insoluble in the aliphatic hydrocarbon, effectively inhibiting  $\text{GaCl}_3$  to be dissolved. Moreover, the formation of  $\text{KGa}_2\text{Cl}_7$  and  $\text{KGa}_3\text{Cl}_{10}$  is also possible, because these species have been observed as well.<sup>46,47</sup>  $\text{NaCl}$  is the most suitable salt for stripping  $\text{GaCl}_3$  because it is easily available, environmentally benign, and cheap. If  $\text{NaCl}$  is used for stripping  $\text{GaCl}_3$ , the resultant  $\text{NaGaCl}_4$  salt can be further processed to recover gallium metal. For instance, it is known that gallium can be electrodeposited from alkaline solutions of  $\text{GaCl}_3$ , so that  $\text{NaGaCl}_4$  could be dissolved in an aqueous  $\text{NaOH}$  solution to prepare an electrolyte for electrodeposition

of gallium metal.<sup>48</sup> The *n*-dodecane after stripping can be recycled and reused for extraction of  $\text{GaCl}_3$ .

## 4. CONCLUSIONS

A preliminary solvometallurgical process using only anhydrous *n*-dodecane and  $\text{NaCl}$  has been developed for the separation of  $\text{GaCl}_3$  and  $\text{AlCl}_3$ , based on the exceptionally high solubility of  $\text{GaCl}_3$  in hydrocarbon solvents and on its Lewis acidity.  $\text{GaCl}_3$  can be efficiently extracted by anhydrous *n*-dodecane from binary solid mixtures of  $\text{GaCl}_3/\text{AlCl}_3$  without formation of ionic compounds by chloride transfer thanks to the similarity of the Lewis acidity of these compounds. The loaded  $\text{GaCl}_3$  in *n*-dodecane can be stripped by  $\text{NaCl}$  by forming  $\text{NaGaCl}_4$ . This solvometallurgical process is essentially different from, and can be supplementary to, the hydrometallurgical processes for  $\text{GaCl}_3$  and  $\text{AlCl}_3$  separations.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.9b00768.

Experimental materials; Raman spectra of different separation residues after solid–liquid extraction of  $\text{GaCl}_3$  by anhydrous *n*-hexane; Raman spectra of solid mixtures after stripping  $\text{GaCl}_3$  by  $\text{LiCl}$ ,  $\text{NaCl}$ , and  $\text{KCl}$ ; extraction and stripping rates (PDF)

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### Notes

The authors declare no competing financial interest.

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