Gallium extraction from Jajarm Bayer process liquor using micro-emulsions

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Abstract
Gallium extraction from Jajarm Bayer process liquor (Jajarm, Iran) was investigated using microemulsions. Also the behavior of aluminum was studied as an impurity. Kelex100 (4-ethyl, 1-methyl, 7-octyl, 8-hydroxyquinolene), iso-decanol and n-butanol, and kerosene were used as the surfactant, co-surfactant, and oil phase, respectively. Ternary phase diagrams were produced using various co-surfactants at different C/S ratios. The results obtained show that Winsor II is the predominant region, and the least area was obtained using iso-decanol at C/S = 4. Using n-butanol or iso-decanol at C/S = 2, 100% of gallium was extracted. The equations of the statistical models for the gallium and aluminum extractions using different co-surfactants were calculated. While the highest gallium extraction (100%) was obtained using n-butanol, due to the high co-extraction of aluminum, the lowest separation and enrichment factors were obtained for this system. The highest separation and enrichment factors were obtained using iso-decanol at C/S = 2. The point with the compositions of X_{AF} = 30, X_{OF} = 20, and X_{C/S} = 50 was found to be a suitable choice, and led to 74% and 14% extractions for gallium and aluminum, respectively. An enrichment factor of 5.28 was obtained.

Keywords: Micro-Emulsion, Gallium, Bayer Process, Jajarm, Solvent Extraction.

1. Introduction
Gallium is an important material that is used in the electronics industry. Its demand in the world market has been increasing due to its applications in semi-conductors, high temperature rectifiers, transistors, batteries, and other devices in which photo effects may be used [1-3]. In the recent years, the main way to obtain gallium in viable conditions for the industry is via extraction as a by-product in the hydrometallurgical process of bauxite, the so-called Bayer process. This process consists of digestion of ores in a highly concentrated solution of sodium hydroxide at a high pressure and temperature. Finally, aluminum is precipitated in the form of hydrate following calcination to the final product [2].

The Bayer process liquor normally builds up in the gallium concentrations of 100-300 ppm depending upon the gallium content of bauxite [4]. Many methods have been developed to extract gallium from the Bayer liquor [3]. The solvent extraction of gallium from the Bayer process liquors has been studied extensively by several authors from both the thermodynamic and kinetic viewpoints [1-6].

Utilization of micro-emulsified systems in the extraction of metallic cations has been a good alternative since they have some characteristics that can make them profitable when compared to the conventional solvent extraction [7-11]. A micro-emulsion is defined as a system formed by the dispersion of micro-droplets of two immiscible liquids, stabilized by an interfacial membrane formed by a surfactant and a co-surfactant. They are thermodynamically stable, homogeneous, and optically isotropic solutions. In an excess amount of oil, the micro-emulsion is oil continuous (Winsor I), and in an excess amount of water, it is said to be water continuous (Winsor II) [12].
Dantas et al. have studied gallium extraction from synthetic Bayer solution in micro-emulsified systems [13]. They compared the two extractants saponified coconut oil (SCO) and 8-hydroxyquinolone (kelex-100). In system I (SCO), the extraction percentages of 85.5% and 35.4% were achieved for gallium and aluminum, respectively, and in system II (kelex-100), the yields were 100% and 99.9%, respectively. The synthetic Bayer liquor used in their experiments contained only gallium and aluminum. Iran Aluminum Company (IRALCo) was the first alumina producer in Iran. Jajarm bauxite mines are located about 10 Km east of Jajarm. The Jajarm alumina plant processes diasporic bauxite into sandy alumina. The technology used for this purpose is known as tube digestion. Abdollahy et al. have proposed a flowsheet for the extraction of gallium from Jajarm Bayer process liquor [1, 14-15]. The process includes two solvent extraction stages in mixer-settler using kelex-100 and tributyl phosphate (TBP). Gallium metal is recovered from the final stripping solution via electrolysis. In this work, gallium extraction from Jaram Bayer process liquor by WII systems, composed of a micro-emulsion phase in equilibrium with an excess of aqueous phase, was studied. The effect of different co-surfactants at different ratios as well as the behavior of aluminum as an impurity were studied.

2. Experimental

2.1. Bayer liquor
Bayer liquor was supplied from Jajarm Alumina Company (Jajarm, Iran). The initial concentrations of gallium and aluminum in the sample were 120 ppm and 32 g/L, respectively.

2.2. Chemicals
Kelex 100 (4-ethyl, 1-methyl, 7-octyl, 8-hydroxyquinolone) was supplied from Nanjing Odyssey, China. n-butanol, iso-decanol, and hydrochloric acid were obtained from Merck, Germany. High-grade kerosene (Density = 0.78 g/cm³ at 20 °C, B.P.=190-250 °C) was obtained from Fluka, Germany.

2.3. Micro-emulsion region determination
Phase diagrams were constructed with the purpose of assessing the influence of the co-surfactant and C/S ratio on the phase behavior. The oil phase was mixed with the surfactant/co-surfactant phase, and the mixture was titrated with sodium hydroxide solution (pH = 12) until it turned clear. The volume of the solution used was then recorded. Titration was continued until the mixture became turbid, and then the volume of the solution was recorded again. The phase diagram was constructed by plotting the amounts of aqueous phase, oil phase, and surfactant/co-surfactant phase used in the experiment.

2.4. Data analysis and iso-response curve plots
Statistical treatment was carried out using the Excel software. The Origin Pro (version 8.6) was used to create the iso-response curves.

2.5. Extraction procedure
For gallium extraction, the micro-emulsion was brought into contact with the Bayer process liquor in a 50-mm beaker using a magnetite stirrer for a pre-determined time. The total volume of liquids was about 30 mm. Afterwards, the mixture obtained was kept under rest for phase separation. The aqueous phase was collected, and the concentrations of gallium and aluminum were determined using an inductively coupled plasma (ICP) spectrophotometer. The extraction percentages were calculated by the following equation:

\[ E = \frac{(W - W^*)}{W} \times 100 \]  

where \( W \) is the initial concentration of metal in the aqueous phase and \( W^* \) is the metal concentration in the aqueous phase after extraction.

3. Results and discussion

3.1. Effect of nature of co-surfactant and C/S ratio on micro-emulsion region
Phase diagrams were constructed using n-butanol and iso-decanol at different co-surfactant to surfactant ratios (Figure 1). As shown, Winsor II was the predominant region. This results obtained could be explained by the high salinity of the Bayer process liquor. Guering and Lindman [16] have demonstrated that increasing the salinity causes a transition between the Winsor regions involving the absorption of oil and rejection of water by the surfactant; this process is a lipophilic exchange. According to Dantas et al. [13], the extraction of metal ions in the Winsor II system is often very effective for the acceleration of extraction as well as the improvement in extractability. Figure 1 shows that iso-decanol allows a smaller micro-emulsion (Winsor IV) region. The longer is the alcohol chain, the smaller is the micro-emulsion region. With an increase in the
co-surfactant chain, a displacement of the alcohol from the membrane to the micro-emulsion nucleus direction occurs causing a non-stabilization of the repulsive forces between the polar heads of the surfactant.

Normally, an increase in the micro-emulsion region (Winsor IV) is observed with an increase in the C/S ratio due to the resultant increase in the amount of co-surfactant, which stabilizes the micelles in the micro-emulsion region [8]. In the present work, the C/S ratios of 2 and 4 were investigated for iso-decanol, and little difference was observed for that micro-emulsion existence domain.

3.2. Extraction results
The extraction method consisted of a mixture of the surfactant, co-surfactant, oil phase, and aqueous phase (Bayer Liquor). The points were chosen within the Winsor II region in order to carry out the extraction study (Figure 1). The co-surfactants of n-butanol and iso-decanol were tested. In the extraction stage, the gallium and aluminum extraction percentages were evaluated, concerning the selectivity study. Table 1 shows the composition of the points and the corresponding extraction percentages.

![Figure 1. Ternary diagrams for systems composed of Bayer process liquor/kerosene/kelex100+alcohol (T=27 °C).](image)

<table>
<thead>
<tr>
<th>Points</th>
<th>Point composition (massic fraction)</th>
<th>Extraction percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>n-Butanol C/S=2</td>
</tr>
<tr>
<td></td>
<td>X_Cn</td>
<td>X_AF</td>
</tr>
<tr>
<td>A</td>
<td>70.0</td>
<td>20.0</td>
</tr>
<tr>
<td>B</td>
<td>45.0</td>
<td>45.0</td>
</tr>
<tr>
<td>C</td>
<td>20.0</td>
<td>70.0</td>
</tr>
<tr>
<td>D</td>
<td>20.0</td>
<td>40.0</td>
</tr>
<tr>
<td>E</td>
<td>20.0</td>
<td>20.0</td>
</tr>
<tr>
<td>F</td>
<td>45.0</td>
<td>20.0</td>
</tr>
<tr>
<td>G</td>
<td>30.0</td>
<td>40.0</td>
</tr>
<tr>
<td>H</td>
<td>27.0</td>
<td>55.0</td>
</tr>
<tr>
<td>I</td>
<td>27.0</td>
<td>25.0</td>
</tr>
<tr>
<td>J</td>
<td>50.0</td>
<td>30.0</td>
</tr>
</tbody>
</table>
3.3. Model for extraction percentages
Based on the experimental results obtained, a statistical treatment was carried out using the Excel software, whose outcome provided the model for the extraction percentages. The results obtained showed that the quadratic-like model was the one that best represented the extraction system. The software provided values for the coefficients of the three studied parameters (X_{OF}, X_{CS}, and X_{aq}) as well as their interactions. Further, the software determined the parameters’ coefficients, determined their significance, and finally calculated the equations of statistically fit models.

3.3.1. Modeling gallium and aluminum extractions
Equations of the statistical models for gallium and aluminum extractions using different co-surfactants are presented in Tables 2 and 3.

<table>
<thead>
<tr>
<th>Table 2. Equations of quadratic models for gallium extraction.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Co-surfactant</strong></td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>n-butanol</td>
</tr>
<tr>
<td>n-butanol</td>
</tr>
<tr>
<td>iso-decanol</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 3. Equations of quadratic models for aluminum extraction.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Co-surfactant</strong></td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>n-butanol</td>
</tr>
<tr>
<td>n-butanol</td>
</tr>
<tr>
<td>iso-decanol</td>
</tr>
</tbody>
</table>

Analyzing the equations in Table 2 shows that for all the systems, the X_{OF}X_{AF}, X_{OF}X_{CS}, and X_{AF}X_{CS} interactions had less effect on the gallium extraction than the single mass fractions (X_{OF}, X_{AF}, and X_{CS}). Comparing the interaction effects on the extraction percentage verifies that the X_{AF}X_{CS} interaction has the most influence, while for n-butanol, the effect of X_{OF}X_{AF} is small, and its effect on the system containing iso-decanol is negative.

From Table 3, it is clear that the effect of X_{OF}X_{AF} interaction is not significant for n-butanol at C/S = 2. However, its effect is small for iso-decanol at C/S = 2. While X_{CS} has the most effect on the aluminum extraction in the systems of n-butanol and iso-decanol at C/S = 2 in a positive way, X_{AF} has the most effect on the aluminum extraction in the system of n-butanol at C/S = 4 in a negative way.

3.3.2. Iso-response curves for extraction percentage
The iso-response curves (Figures 2 and 3) were built from the extraction equations (E%), described in Tables 2 and 3. They allowed a better evaluation of the behavior of the extraction yield within the studied domain. Figures 2 and 3 are useful to better understand how the choice of the systems affects the results of gallium and aluminum extractions.

According to Figure 2, using all the three micro-emulsion systems gives the best extraction percentages for the gallium range of 95-100%. However, n-butanol at C/S = 2 has more effect on the Ga extraction. The best results were found by increasing the value for massic fraction of C/S.

Figure 3 shows that higher extraction percentages were obtained for aluminum using n-butanol as a co-surfactant. The extraction percentage increased with increasing C/S.

The equations of the models were tested for some points, and their experimental and calculated values were tabulated in Table 4.

In some cases, a high deviation was encountered for aluminum due to the high concentration of the metal in the aqueous phase after extraction, favoring the precipitation and making the experiment reproducibility difficult.
3.3.3. Iso-response curves for separation and enrichment factors

From an industrial point of view, gallium recovery from Bayer liquor requires a selective extraction method in order to separate it from aluminum. When two metal ions are to be extracted from an aqueous solution by an organic solvent, the separation factor, $\beta$, of these ions is defined by [17]:

$$\beta = \frac{D_A}{D_B}$$

where $D_A$ and $D_B$ are the distribution coefficients of the two metals. For the separation to be
possible, β must not equal 1. The enrichment factor, E, is given by [17]:

$$E = \frac{\text{Percent extraction of } A}{\text{Percent extraction of } B} = \frac{D_B + \frac{V_A}{V_o}}{D_A + \frac{V_A}{V_o}}$$  (3)

To have a high enrichment, therefore, not only the separation factor must be high but also the aqueous/organic ratio should be taken into consideration. Also the volume of the organic phase should be as small as possible compared to the aqueous phase [17].

To evaluate the performance of each system, the separation and enrichment factors were calculated, and the iso-response curves were plotted using the equations of statistical models (data not shown). As illustrated in Figure 4, the highest separation and enrichment factors were obtained at C/S = 2 using iso-decanol, while the highest gallium extraction (100%) was obtained using n-butanol as a co-surfactant, and low separation and enrichment factors were obtained for this system because of high co-extraction of Al.

The best composition for the extraction should be chosen in a way that the final goal of maximum gallium extraction is obtained via the highest enrichment factor. For example, using iso-decanol, the point with the composition of $X_{AF} = 30$, $X_{OF} = 20$, and $X_{C/S} = 50$ is a suitable choice, and leads to 74% and 14% extractions for gallium and aluminum, respectively. The related enrichment factor was 5.28.

3.4. Aluminum scrubbing and gallium stripping

Once gallium and aluminum were extracted by the micro-emulsion, scrubbing of aluminum and stripping of gallium were done. The method and conditions were based upon an early work by Abdollahy et al. [2].

First the loaded organic phase was brought into contact with a 6 M HCl solution. Then the micro-emulsion after aluminum scrubbing was mixed with 1.5 M HCl solution. The organic/aqueous phase ratio was 1. The results obtained showed that about 95% of gallium was stripped out.

### Table 4. Validity test of quadratic models for extraction percentage (E%) of aluminum and gallium.

<table>
<thead>
<tr>
<th>Co-surfactant type and C/S ratio</th>
<th>Points</th>
<th>Experimental values (%)</th>
<th>Calculated values (%)</th>
<th>Experimental values (%)</th>
<th>Calculated values (%)</th>
<th>Deviation Al</th>
<th>Deviation Ga</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-butanol; C/S=2</td>
<td>A</td>
<td>100.00</td>
<td>98.79</td>
<td>96.54</td>
<td>100.00</td>
<td>3.46</td>
<td>1.21</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>85.72</td>
<td>85.84</td>
<td>33.52</td>
<td>29.76</td>
<td>3.76</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>85.60</td>
<td>83.29</td>
<td>21.85</td>
<td>32.00</td>
<td>10.15</td>
<td>2.31</td>
</tr>
<tr>
<td>n-butanol; C/S=4</td>
<td>A</td>
<td>95.46</td>
<td>97.40</td>
<td>91.13</td>
<td>90.89</td>
<td>0.24</td>
<td>1.94</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>50.00</td>
<td>53.70</td>
<td>27.71</td>
<td>21.24</td>
<td>6.47</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>15.40</td>
<td>15.25</td>
<td>29.98</td>
<td>17.19</td>
<td>12.79</td>
<td>0.15</td>
</tr>
<tr>
<td>iso-decanol; C/S=2</td>
<td>A</td>
<td>95.50</td>
<td>94.58</td>
<td>91.10</td>
<td>90.89</td>
<td>0.21</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>55.00</td>
<td>51.10</td>
<td>27.70</td>
<td>21.24</td>
<td>6.46</td>
<td>3.90</td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>37.00</td>
<td>46.05</td>
<td>96.60</td>
<td>54.35</td>
<td>42.25</td>
<td>9.05</td>
</tr>
</tbody>
</table>

Figure 4. Isoreponse curves for 1) separation and 2) enrichment factors of different systems.

a) n-butanol at C/S = 2, b) n-butanol at C/S = 4, and c) iso-decanol at C/S = 2.
4. Conclusions
Gallium extraction from Jajarm Bayer process liquor (Jajarm, Iran) was investigated using micro-emulsions. Kelex100, iso-decanol and n-butanol, and Kerosene were used as the surfactant, co-surfactant, and oil phase, respectively. Ternary phase diagrams were produced using various co-surfactants at different C/S ratios. The results obtained showed that Winsor II was the predominant region, and the least area was obtained using iso-decanol at C/S = 4. Using n-butanol or iso-decanol at C/S = 2, 100% of gallium was extracted. Equations of statistical models for gallium and aluminum extractions were obtained using different co-surfactants. It was found that single mass fractions (X_{OF}, X_{AF}, and X_{CS}) had more effects on Ga and Al extractions than the X_{OF}X_{AF}, X_{OF}X_{CS} and X_{AF}X_{CS} interactions. While the highest gallium extraction of 100% was obtained using n-butanol as the co-surfactant, the lowest separation and enrichment factors were obtained for this system because of the high co-extraction of Al. The highest separation and enrichment factors were obtained using iso-decanol at C/S = 2. The point with the composition of X_{AF} = 30, X_{OF} = 20, and X_{CS} = 50 is a suitable choice, and will lead to 74% and 14% extractions for gallium and aluminum, respectively. The enrichment factor will be 5.28.

Acknowledgments
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References

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استخراج با حلال گالیم از محلول بایر حاصل از کارخانه جاجرم با استفاده از روش میکرو امولسیون

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چکیده:
در این تحقیق، استخراج گالیم از محلول بایر حاصل از کارخانه آلومینای جاجرم با استفاده از روش میکرو امولسیون بررسی شد. همچنین رفتار آلومینیوم به عنوان مهم‌ترین ناخالصی مطالعه شد. کلکس ۱۰۰۰ از دکانول و بوتانول کور زین به جای سطح ساز و فاز روغنی استفاده شده، دی‌آگرامهای سه‌ای با استفاده از سطح سازهای مختلف در نسبت‌های مختلف C/S ترسیم شدند. نتایج نشان داد که وینسور II ناحیه غالب در دی‌آگرامهای سه‌ای اسیت و کمترین وسعت آن با دکانول در C/S به دست آمده با استفاده از بوتانول یا دکانول در C/S = ۴/۰۰۰/۹۱/۰ و C/S = ۰/۳۰۰/۷۴/۰٪ گالیم استخراج می‌شود. مدل رگرسیونی برای استخراج گالیم و آلومینیوم با سطح سازی مختلف تعیین شد. از این نتیجه نشان می‌دهد، با استفاده از عناصر با دکانول و در C/S = ۶/۲ و C/S = ۶/۲ کمترین نکات در استخراج گالیم و آلومینیوم با سطح سازی مختلف تعیین شد. در این حالت، مکاتبات در XCS = ۴۰، XAF = ۲۰، XDF = ۴۰، XOF = ۳۰ و XCF = ۷۴/۰٪ آلومینیوم می‌شود. فاکتور جدایی در XCS = ۴۰/۲ و XAF = ۴۰/۳ است.

کلمات کلیدی: میکرو امولسیون، گالیم، فاز بایر، جاجرم، استخراج با حل‌آلول