Droplet fractionation of hexavalent chromium from bubbles bursting at liquid surfaces of chromic acid solutions

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Abstract

The aim of this study was to evaluate the effects of electrolyte concentration and gassing rate (in terms of gas flow rate) on the droplet fractionation of Cr(VI) from bubbles bursting at liquid surfaces of chromic acid solutions. An experimental system was used to generate gas bubbles in solutions, and the droplets thus generated were measured by an aerodynamic particle sizer (APS). A Marple personal impactor was used simultaneously to collect droplet samples for chemical analysis. Ratios of the Cr(VI) concentration in droplets to that in the bulk solution were calculated to evaluate the droplet fractionation effect. The results showed that the concentration ratios had a range of about 5 to less than unity for the experimental conditions used in this study, indicating that the droplets can be either enriched or depleted with Cr(VI) relative to the bulk solution. The concentration ratio decreased exponentially with increasing electrolyte concentration, but decreased approximately linearly with increasing gas flow rate. In addition, surface tension also played an important role in chemical fractionation by droplet formation from bursting bubbles. The results should have applications in assessing the health risk of chromium electroplating plants where chromium-containing droplets are generated as a result of electrochemical reactions and gassing. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Droplets; Bursting bubbles; Chromium electroplating; Chemical fractionation

1. Introduction

Bursting of single bubbles at liquid surfaces results in the formation of both film droplets and jet droplets. When a gas bubble in a liquid rises to the surface, it forms a hemispheric film cap...
above the surface. The bubble stays on the surface for a short time as a result of the equilibrium between buoyancy and surface tension forces. The film cap becomes thinner because of liquid drainage and breaks into numerous droplets, termed film droplets, in a variety of sizes when its thickness reaches a certain critical value. Generally, film droplets are generated several hundred microseconds after a bubble ruptures (Resch, 1986). Immediately following the breakage of a bubble, the surrounding liquid fills the remaining bubble cavity and a liquid jet appears in the center of the crater. The jet rising upward from the collapsing bubble cavity is unstable and soon breaks into a few large droplets, named jet droplets (Newitt, Dombrowski, & Knelman, 1954).

Droplet generation by bubbles bursting at liquid surfaces is a common phenomenon in many natural processes (such as sea sprays) and industrial processes (such as metal electroplating and anodizing processes). It plays an important role in the liquid-to-air transfer of biological, nonvolatile chemical, and even radioactive substances, which may have adverse effects on the environment and human health (Blanchard & Syzdek, 1970; Van Grieken, Johansson, & Winchester, 1974; Piotrowicz, Duce, Fasching, & Weisel, 1979; Burger & Bennett, 1985). Studies focused on the transfer of trace metals from seawater to air by bursting bubbles showed that oceanic droplets were enriched with trace metals such as Fe, Cu, and Zn with respect to Na (Van Grieken et al., 1974; Piotrowicz et al., 1979). These studies dealt with the liquid-to-air transfer of the trace substances. Little is known regarding the transfer of ions from concentrated solutions to air by bursting of bubbles as often seen in some industrial processes.

Among all kinds of metal electroplating, chromium electroplating has the lowest current efficiency, with 80–90% of the applied current consumed in the dissociation of water (Burgess, 1995). The hydrogen and oxygen gases thus produced emerge in the form of gas bubbles and burst into droplets containing chromium ions at the liquid surface. Most chromium electroplating factories use toxic Cr(VI) (in the form of chromic acid) instead of non-toxic Cr(III) on account of its cost. Droplets containing Cr(VI) are considered to be the main cause of nasal septum diseases among chromium electroplating workers (Gomes, 1972; Lindberg & Hedenstierna, 1983; Lin, Tai, Chan, & Wang, 1994). This study was aimed at evaluating the fractionation of Cr(VI) in droplets generated from bubbles bursting at liquid surfaces of chromic acid solutions by an experimental system. The parameters studied included the concentration of chromic acid and the gassing rate in terms of gas flow rate. The droplet fractionation of Cr(VI) was expressed by the ratio of the Cr(VI) concentration in droplets to that in the bulk solution.

2. Materials and methods

Five different concentrations of chromic acid solution, 31.25, 62.5, 125, 250 and 375 kg m⁻³, were used in this study to cover the electrolyte concentration levels employed in practical applications. The physical properties of tested solutions are listed in Table 1. The density of the solutions was determined by a weighing method. The surface tension and the viscosity of the solutions were measured by a tensionmeter (Model k12, Kruss, Hamburg, Germany) and a capillary viscometer (Ubbelohde Micro Viscometer, capillary No. 5010a, Scott Geräte, Mainz, Germany), respectively. Measurements of these properties were made at the same temperature and pressure (45°C, 1 atm) as in the experiments.
Table 1
The physical properties of test solutions at 45°C, 1 atm^a^

<table>
<thead>
<tr>
<th>CrO\textsubscript{3} concentration in the bulk solution (kg m\textsuperscript{-3})</th>
<th>31.25</th>
<th>62.5</th>
<th>125</th>
<th>250</th>
<th>375</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg m\textsuperscript{-3} × 10\textsuperscript{3})</td>
<td>1.021</td>
<td>1.044</td>
<td>1.087</td>
<td>1.177</td>
<td>1.265</td>
</tr>
<tr>
<td>Surface tension (N m\textsuperscript{-1} × 10\textsuperscript{-2})</td>
<td>6.515</td>
<td>6.593</td>
<td>6.697</td>
<td>6.823</td>
<td>6.955</td>
</tr>
<tr>
<td>Viscosity (kg m\textsuperscript{-1} s\textsuperscript{-1} × 10\textsuperscript{-4})</td>
<td>6.2</td>
<td>6.4</td>
<td>6.4</td>
<td>6.8</td>
<td>7.4</td>
</tr>
</tbody>
</table>

^a^The surface tension of water is 6.878 × 10\textsuperscript{-2} N m\textsuperscript{-1} at 45°C.

The experimental setup consisted of a glass cylindrical tank, a water bath, a bubbling system, and the droplet sampling/measuring instruments (see Kuo & Wang, 1999 for details). In an electroplating process, bubbles are formed from gases produced by electrolysis as well as from gases introduced into the electroplating tank for agitation purposes. To simulate such a gas bubbling process, filtered and humidified air was introduced into solution through capillary tubes placed at the experimental tank used in this study. The bubbles produced under all the experimental conditions were about 2 × 10\textsuperscript{-3} m in diameter. To provide a sufficient gas flow for sampling by the aerosol instruments, the air should be supplied at a rate greater than 6.7 × 10\textsuperscript{-5} m\textsuperscript{3} s\textsuperscript{-1} (= 41 min\textsuperscript{-1}). On the other hand, the air flow rate should not exceed 1.3 × 10\textsuperscript{-4} m\textsuperscript{3} s\textsuperscript{-1} (= 81 min\textsuperscript{-1}) in order to avoid the coalescence of bubbles during rising through the liquid. With the experience of our previous study (Kuo & Wang, 1999), the tested electrolyte solutions were freshly prepared to avoid rapid accumulation of a foam layer at the liquid surface. In each run, the chromic acid solution of a given concentration was prepared with deionized distilled water and then heated to 45°C in a storage container placed in a temperature-controlled water bath. Air was then introduced into the bubbling system at a flow rate of 6.7 × 10\textsuperscript{-5}, 1.0 × 10\textsuperscript{-4}, 1.3 × 10\textsuperscript{-4} m\textsuperscript{3} s\textsuperscript{-1} (= 4, 6 or 81 min\textsuperscript{-1}). The electrolyte solution was then gradually transferred to the bubbling tank by a peristaltic pump (Model 505S, Watson Marlow, Falmouth, UK) until the liquid height reached a constant level of 0.15 m above the capillary openings.

An eight-stage Marple personal impactor (Model 290, Graseby Andersen, Atlanta, GA, USA), with aerodynamic cutoff diameters of 0.6, 1, 1.5, 3.5, 6, 10, 15, 21 μm at a sampling flow rate of 3.3 × 10\textsuperscript{-5} m\textsuperscript{3} s\textsuperscript{-1} (= 21 min\textsuperscript{-1}), was used to collect size-fractionated droplet samples on polyvinyl chloride filters (34 mm, 5 μm pore size, Omega Specialty Instrument Co., Chelmsford, MA, USA) for analysis of Cr(VI). The backfilter of the impactor for collecting droplets smaller than 0.6 μm was not used because the pores were often plugged during sampling. The US National Institute for Occupational Safety and Health (NIOSH) Method 7600 was employed to determine the Cr(VI) concentration in each droplet sample. The method utilizes the reagent 2-diphenylcarbazide which reacts specifically with Cr(VI) to form a purple-red color complex. The instrumental detection limit was 1.8 × 10\textsuperscript{-6} kg m\textsuperscript{-3} (equivalent to 9 × 10\textsuperscript{-12} kg m\textsuperscript{-3} for a 0.24 m\textsuperscript{3} air sample). Recovery of Cr(VI) was determined by adding a spiked aqueous solution of potassium dichromate on PVC filters. The percentages of recovery at 10\textsuperscript{-9} and 10\textsuperscript{-8}-kg concentration levels were 97 ± 3% and 95 ± 3%, respectively, within 54000 s (= 15 h) after spiking.
The relative standard deviation of the measurements, defined as the ratio of the standard deviation and the mean of the replicates, was 0.060 ± 0.001, indicating the excellent precision of the measurements. An alternative method of analysis is to suspend single droplets in electrodynamic balances in a flow of air and use Raman spectroscopy to identify Cr(VI) in the droplets. Foss, Allen, Blair, and Davis (1993) have used such an approach to analyze chromic acid droplets from an anodizing tank.

An aerodynamic particle sizer (Model 3310, TSI, St. Paul, MN, USA) was employed to measure the number concentration and size distribution of the droplets in the aerodynamic size range of 0.8–30 μm. The sampling probes of the Marple personal impactor and the APS were placed in parallel at 0.35 m above the liquid surface. In each run, airborne droplets were sampled by the Marple personal impactor for a duration of 7200 s (= 2 h) and, simultaneously, the number concentration of droplets was measured by the APS three times.

3. Results and discussion

3.1. Size-fractionated Cr(VI) concentrations in droplets

A representative distribution of the Cr(VI) concentration in droplets is shown by bar plots in Fig. 1. In general, the Cr(VI) mass distributions were bimodal with a mode at a diameter larger than 10 μm and another at about 3–5 μm. The peak above 10 μm, which represented the contribution of jet droplets, moved to larger diameters as the CrO₃ concentration in bulk solution increased.

The airborne Cr(VI) mass concentrations in droplets larger than 1 μm in aerodynamic diameter are listed in Table 2. Under the experimental conditions studied, the airborne Cr(VI) concentration varied from $3.2 \times 10^{-8}$ to $1.57 \times 10^{-7}$ kg m⁻³. For a given gas flow rate, there was a maximum airborne Cr(VI) concentration at a certain electrolyte concentration.

For CrO₃ concentrations in bulk solution higher than $125$ kg m⁻³, the airborne Cr(VI) concentration increased markedly with increasing gas flow rate, except at a gas flow rate of $1.3 \times 10^{-4}$ m³ s⁻¹ (= 81 min⁻¹) in a solution of $375$ kg m⁻³ CrO₃, for which foam formed on the liquid surface gradually during the experiment. At lower electrolyte concentrations (i.e., 31.25 and $62.5$ kg m⁻³ CrO₃), the Cr(VI) concentration in droplets appeared to have a maximum in the range of the gas flow rates studied.

3.2. Droplet volume distributions

The droplet volume distributions were calculated from the number distribution data measured by the APS. To calculate the droplet volume, the droplet aerodynamic diameter was first converted to a physical diameter by

$$d_{ae} = d_v \left[ \frac{\rho_p C(d_v)}{\rho_0 C(d_{ae})} \right]^{1/2},$$
Fig. 1. The airborne Cr(VI) mass distribution (shown by bar plots) and the corresponding droplet volume distribution (shown by open circles and lines) at a gas flow rate of $6.7 \times 10^{-5}$ m$^3$ s$^{-1}$ ($=41$ min$^{-1}$) in a solution of 250 kg m$^{-3}$ CrO$_3$.

Table 2

<table>
<thead>
<tr>
<th>Gas flow rate (m$^3$ s$^{-1}$)</th>
<th>CrO$_3$ concentration in the bulk solution (kg m$^{-3}$)</th>
<th>Airborne Cr(VI) conc.</th>
<th>Droplet volume conc.</th>
<th>Airborne Cr(VI) conc.</th>
<th>Droplet volume conc.</th>
<th>Airborne Cr(VI) conc.</th>
<th>Droplet volume conc.</th>
<th>Airborne Cr(VI) conc.</th>
<th>Droplet volume conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>31.25</td>
<td>32 ± 6</td>
<td>299 ± 79</td>
<td>62.5</td>
<td>72 ± 6</td>
<td>654 ± 124</td>
<td>463 ± 100</td>
<td>125</td>
<td>73 ± 19</td>
</tr>
<tr>
<td></td>
<td>62.5</td>
<td>85 ± 23</td>
<td>55 ± 16</td>
<td>125</td>
<td>250</td>
<td>129 ± 9</td>
<td>135 ± 17</td>
<td>250</td>
<td>55 ± 16</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>109 ± 10</td>
<td>1080 ± 45</td>
<td>129 ± 9</td>
<td>375</td>
<td>1107 ± 142</td>
<td>793 ± 196</td>
<td>135 ± 17</td>
<td>793 ± 196</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>128 ± 5</td>
<td>1175 ± 123</td>
<td>157 ± 18</td>
<td>123 ± 9</td>
<td>1479 ± 146</td>
<td>923 ± 224</td>
<td>123 ± 9</td>
<td>1311 ± 167</td>
</tr>
<tr>
<td></td>
<td>375</td>
<td>1145 ± 170</td>
<td>793 ± 196</td>
<td>123 ± 9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

where $d_{ae}$ is the aerodynamic diameter, $d_v$ the equivalent volume diameter, $\rho_p$ the droplet density, $\rho_0$ the unit density (10$^3$ kg m$^{-3}$), $C$ the slip correction factor, and $\chi$ the dynamic shape factor. The droplet density was assumed to be identical to the density of the original solution. Both $C$ and $\chi$ have a value of one for relatively large spherical droplets.

The droplet volume concentration in a given size interval was determined by multiplying the volume of a droplet with the geometric mean diameter by the number concentration in the given size interval ($\pi d_g^3 N / 6$, where $d_g$ is the geometric mean diameter and $N$ the number concentration of droplets in a given size range).

Fig. 1 also shows the corresponding droplet volume distribution by open circles and lines. The droplet volume distribution was clearly bimodal, indicating the presence of both film and jet droplets. The film droplet mode was in the size range of 3–5 μm while the jet droplet...
mode was in the size range of 10–15 μm. Although there was no sharp separation between film and jet droplets in the measured size distributions, droplets larger than 7 μm were presumably jet droplets whereas those smaller than 7 μm were considered to be film droplets. In general, the droplet volume distributions were comparable in shape to the corresponding Cr(VI) mass distributions for all the measurements.

Table 2 also lists the volume concentrations of droplets larger than 1 μm in aerodynamic diameter. Under the experimental conditions studied, the droplet volume concentration varied from about $3 \times 10^8$ to around $1.5 \times 10^9$ μm$^3$ m$^{-3}$. The droplet volume concentration distributed approximately lognormally with respect to the electrolyte concentration. There is no clear explanation for this because of the limited data of the present study. However, this may be attributed to the effect of liquid properties such as surface tension and density. Parachristodoulou, Foulkes, and Smith (1985) reported that jet droplets decreased with decreasing surface tension and increasing density of the liquid phase.

3.3. Concentration ratios of Cr(VI) in droplets to Cr(VI) in the bulk solution

Concentration ratios of Cr(VI) in droplets to Cr(VI) in the bulk solution were calculated to evaluate the effects of parameters such as electrolyte concentration and gas flow rate on the droplet fractionation of Cr(VI). The Cr(VI) concentration in droplets was obtained by dividing the airborne Cr(VI) concentration by the droplet volume concentration in a given size interval while the Cr(VI) concentration in the bulk solution was estimated by multiplying the CrO$_3$ concentration in the bulk solution by a factor of 0.52 (the molecular weights of CrO$_3$ and Cr(VI) are 100 and 52, respectively).

To obtain a better estimate of the Cr(VI) concentration in droplets, only the Cr(VI) concentration in the droplets of 1–10 μm in aerodynamic diameter was calculated because both the Marple personal impactor and the APS progressively underestimate the concentration of droplets beyond 10 μm. For the Marple personal impactor, the sampling efficiency was nearly 100% for 10-μm particles, but declined to about 80% for particles larger than 21 μm (Rubow, Marple, Olin, & McCawley, 1987; Rader, Mondy, Brockmann, Lucero, & Rubow, 1991). The APS increasingly undersampled droplets with increasing droplet size because of decreasing inlet efficiency. Kinney and Pui (1995) found that the APS sampled particles smaller than 10 μm with an efficiency of nearly 100%, whereas the efficiency dropped from around 80% for 20-μm particles to less than 60% for particles larger than 30 μm.

Table 3 lists the Cr(VI) concentrations in droplets of 1–10 μm aerodynamic diameter under all experimental conditions. At a given gas flow rate, the droplet Cr(VI) concentration was generally higher for those generated by bubbles bursting from solutions of higher electrolyte concentrations than those from solutions of lower concentrations. However, the droplet Cr(VI) concentration was not proportional to the electrolyte concentration of the bulk solution. It appears that the Cr(VI) ions in droplets tended to reach a saturated concentration as the electrolyte concentration in bulk solution increased.

Table 3 also shows that the droplet Cr(VI) concentration decreased with increasing gas flow rate for a given concentration of electrolyte solution. As a bubble formed in a solution, the ions in the solution tended to adsorb to the thin liquid layer surrounding the bubble. When the bubble film cap burst into droplets, the Cr(VI) ions in the resulting film droplets came from
Table 3
The Cr(VI) concentrations (in kg m\(^{-3}\)) in droplets of 1–10 \(\mu\)m in aerodynamic diameter under all experimental conditions

<table>
<thead>
<tr>
<th>Gas flow rate (m(^3) s(^{-1}))</th>
<th>CrO(_3) concentration in the bulk solution (kg m(^{-3}))</th>
<th>CrO(_3) concentration in the bulk solution (kg m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.25</td>
<td>85 ± 10</td>
<td>85 ± 11</td>
</tr>
<tr>
<td>62.5</td>
<td>64 ± 7</td>
<td>69 ± 11</td>
</tr>
<tr>
<td>125</td>
<td>31 ± 2</td>
<td>38 ± 1</td>
</tr>
<tr>
<td>250</td>
<td>85 ± 11</td>
<td>83 ± 8</td>
</tr>
<tr>
<td>375</td>
<td>96 ± 2</td>
<td>100 ± 8</td>
</tr>
<tr>
<td></td>
<td>151 ± 14</td>
<td>112 ± 11</td>
</tr>
<tr>
<td></td>
<td>168 ± 44</td>
<td>107 ± 11</td>
</tr>
</tbody>
</table>

The ions in the bubble film. For a given electrolyte concentration, the bubble production rate increased as the gas flow rate increased (not in proportion because the bubble size may change as well) and, as a result, the average number of ions in the thin film carried by a bubble decreased. This may explain why the droplet Cr(VI) concentration decreased with increasing gas flow rate.

Fig. 2 plots the concentration ratio against the electrolyte concentration in bulk solution for all experimental conditions. In general, the concentration ratio decreased exponentially with increasing electrolyte concentrations. For a given gas flow rate, the concentration ratio decreased exponentially as the bulk electrolyte concentration increased. A concentration ratio higher than unity indicates that the droplets are enriched with Cr(VI) ions by bubble bursting. It can be seen from Fig. 2 that the droplets generated from dilute solutions were enriched with Cr(VI) ions.
ions, whereas those from concentrated solutions were depleted of the ions. This finding may have health implications for chromium electroplating workers.

Fig. 3 shows that the concentration ratio decreased as the surface tension increased. The surface tension of the solution appears to play an important role in the droplet fractionation of Cr(VI) by bursting bubbles.

Fig. 4 shows the effect of gas flow rate on the concentration ratio for all experimental conditions. The concentration ratio decreased markedly with increasing gas flow rate for lower electrolyte concentrations but not for higher concentrations. This may be attributable to the higher ion concentrations in solutions of higher electrolyte concentrations. In a solution of higher electrolyte concentrations, the liquid region depleted of ions by scavenging bubbles can be quickly resupplied by ions from nearby regions.

4. Conclusions

Droplet fractionation plays an important role in the liquid-to-air transport of hazardous substances. The fractionation process may be influenced by a number of factors such as liquid properties, gassing rate, bubble size, and the bubble rising distance. The present study has demonstrated the effects of electrolyte concentration and gassing rate in terms of the gas flow rate on the droplet fractionation of hexavalent chromium from bubbles bursting at liquid surfaces of chromic acid solutions. The following conclusions can be drawn for the studied ranges of electrolyte concentration and gas flow rate.
At a given gas flow rate, the droplet Cr(VI) concentration was generally higher for those generated by bubbles bursting from solutions of higher electrolyte concentrations than those from solutions of lower concentrations. However, the concentration ratio (droplet to bulk solution) decreased exponentially with increasing electrolyte concentrations. Liquid properties, especially the surface tension, appeared to play an important role in the droplet fractionation of Cr(VI) by bursting bubbles.

The droplet Cr(VI) concentration decreased with increasing gas flow rate for a given concentration of electrolyte solution. The concentration ratio decreased markedly with increasing gas flow rate for lower electrolyte concentrations but not for higher electrolyte concentrations.

Other factors such as liquid properties, bubble size, and the bubble rising distance may have effects on the droplet fractionation. To obtain a better understanding of the droplet fractionation mechanism, additional studies on the effects of these factors are needed.

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References


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