Rationalizing Nonideal Results from Undivided-Cell Electrowinning Experiments

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Abstract: The appropriate interpretation of mass-balance data from undivided-cell electrowinning experiments allows for the determination of some simple aspects of metal-cation speciation within the electrolysis solution. The data that needs to be collected is limited to the ratio of the amount of acid produced to the amount of metal removed from the solution. By analysis of a simplified model of the electrowinning experiment, the ability to use such data to determine certain limits of metal-cation speciation is demonstrated. The overall treatment is useful in demonstrating to chemistry students that significant conclusions can be drawn from easily collected data when the system under consideration is well-understood.

Introduction

Electrowinning is the process whereby an aqueous solution of a metal salt is subjected to electrolysis such that metal is electrodeposited on the cathode and $H^+(aq)/O_2(g)$ is generated at the anode. Through electrowinning, elemental metal can be won (recovered) from an aqueous solution of the appropriate metal salts (i.e., salts of those metals that can be electrodeposited from aqueous solution). Electrowinning is used extensively in the commercial production and recovery of pure metals from ore and scrap. For example, the electrowinning of copper from aqueous copper sulfate solutions is employed as the final step in the production of pure copper from ore. In addition to elemental metal, the conjugate acid of the metal salt's anion is also produced during the electrowinning process, and such acid is almost always recycled for further use within commercial operations that employ electrowinning. For example, the sulfuric acid generated by the electrowinning of copper from an aqueous copper sulfate solution can be reused for the heap leaching of more copper sulfate from an ore pile. By use of the term "undivided cell" one refers to an electrochemical cell wherein the anode and cathode are continuously exposed to the same solution. This is to be contrasted with a divided cell wherein some sort of ionically conductive separator (e.g., glass frit, asbestos pad, ion-selective membrane) is used to separate the cell into an anode chamber and a cathode chamber. Undivided cells are generally the cheapest to build, operate, and maintain, but divided cells allow for improved product purity and for a greater range of possible electrochemical processes.

The Undivided-Cell Electrowinning Experiment

The simplest electrowinning experiment involves taking an aqueous solution of an appropriate metal salt in an undivided cell equipped with an inert anode (i.e., an anode that will decompose the H_2O solvent as opposed to dissolving in it; IrO_2-coated titanium is ideal) and an appropriate cathode (e.g., copper panel) and subjecting this solution to electrolysis at a reasonable voltage for a reasonable length of time. The expected result of the experiment is that metal will have been depleted from the aqueous solution while acid will have been produced. The quantitative result of the experiment can be simply obtained by removing the anode and cathode, filtering the remaining solution to remove all suspended solids (e.g., to remove flakes of the cathode deposit that broke off into the solution), weighing the filtered solution to correct for evaporation during the experiment, and, finally, analyzing the solution for total metal and total acid content. By monitoring the ratio of the decrease in metal content to the increase in acid content as a function of the solution composition and the electrowinning conditions, one can quantitatively optimize the electrowinning process. Such optimization of the electrowinning process is useful in commercial applications, and it is the purpose of this paper to describe a basic electrowinning experiment and also to provide some suggestions for the interpretation of nonideal undivided-cell electrowinning data [1].

The undivided-cell electrowinning process is shown diagrammatically in Figure 1.

Generic instructions for an undivided-cell electrowinning experiment. Fill an undivided cell (a box) with a weighed amount of an aqueous solution of a salt (e.g., AgOMs, $CuSO_4$) that has an anion that is not electrochemically reactive (e.g., do not use NO_3^-, which is reduced on the cathode, or Cl^-, which is oxidized on the anode). Characterize the solution with respect to acid and metal content. The metal content is most easily measured by atomic absorption spectroscopy (AA). The acid content of the solution is best analyzed by pH titration.

Assemble the cell and electrolyze at a voltage that generates a cathodic current density of about 50 ASF (amps per square foot). Continue the electrolysis for a time that allows at least 80%, and more preferably over 99%, of the metal to be removed. The current density is calculated by dividing the current passed by the exposed electrode area. The electrolysis time, t, can be calculated in seconds for a 100% efficient process as $t = FMVn/I$ (F = 96,500 coulombs per mole of electrons, M = molarity of the metal, V = solution volume, I = current applied, n = metal valence).

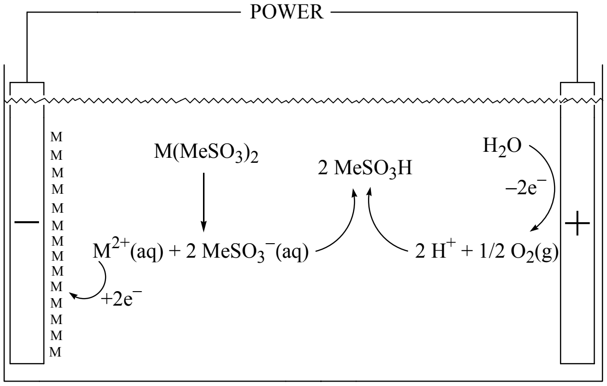

Figure 1. The undivided-cell electrowinning process. The electrolyte employed here is aqueous methanesulfonic acid, and $M(MeSO_3)_2$ refers to an arbitrary metal methanesulfonate. The overall reaction can be represented as $M(MeSO_3)_2(aq) + H_2O \rightarrow 2\ MeSO_3H(aq) + M(s) + ½\ O_2(g)$. The squiggly line in the picture above represents the solution surface.

Remove the electrolyzed solution, filter out insoluble material, and weigh the filtrate.

Analyze the filtrate for total dissolved metal content (e.g., by AA) and total acid content (e.g., by pH titration).

Determine the total amount of metal removed from the solution and the total amount of acid produced in the solution. Divide the moles of acid produced in the solution by the moles of metal removed from the solution to get a figure of merit for the overall process. We will refer to this value as the APR (acid-production ratio) for the experiment.

Specific Experimental Instructions

An undivided electrowinning cell (e.g., a 500-ml beaker) was charged with 250 ml of $Cu(OMs)_2(aq)$ solution [52 g/L as Cu metal]. The cell is fitted with a copper cathode (exposed geometric area = 6 in^2) and an IROX anode (exposed geometric area = 5 in^2). IROX anodes (IrO_2-coated titanium) are available from a number of suppliers (e.g., ELTECH of Chardon, Ohio and Electrode Products of Warren, NJ). The IROX anodes we employed were meshes that had electrochemical surface areas equal to the geometric area of the entire piece. A constant current of 4 A was passed through the cell for 3 h followed by a constant current of 2 A for 1 h. The cell voltage hovered at about 5 V throughout the electrolysis. A total of 50,400 C of charge was passed (14 Ah = 50,400 coulombs = 0.52 mol of e^-). The volume of the solution was maintained throughout the experiment by additions of DI water. The copper concentration was reduced from an initial level of 52 g/L [as Cu] to a final value of 0.3 g/L [as Cu] (approximately an 0.8 M decrease in [Cu]) while the MSA(aq) concentration was increased from approximately 0 g/L up to 134 g/L (approximately 1.4 M increase in acid). The cathode process was approximately 80% efficient for the reduction of copper. The APR is defined as the ratio of the acid produced to the metal removed, and for this experiment the APR was calculated as 0.35 moles $H^+ \div 0.2$ moles Cu = 1.75 (less than the theoretically expected value of 2). A possible explanation for the low APR could invoke partial cathodic reduction of $Cu^{2+}(aq)$ to insoluble $Cu^{1+}(s)$. An APR of 1 would be expected for this process, and by allowing for some $Cu^{2+}(aq) \rightarrow Cu^+(s)$ reduction, one can rationalize an APR < 2.

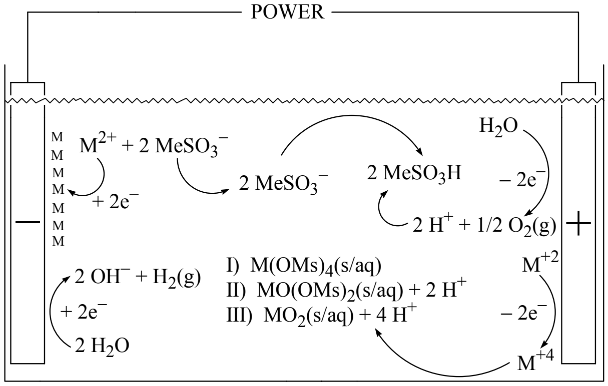

Figure 2. The undivided electrowinning process shown in Figure 1 with reactions added to display the nonideal processes that occur on the anode and cathode. Because the experimental work done as part of this study (experimental results to be discussed later) employed metal methanesulfonate salts, we will designate solution-soluble species as methanesulfonates (mesylates) using OMs, $MeSO_3$, or CH_3SO_3 to designate the methanesulfonate anion.

Real Electrowinning Experiments

Electrowinning APRs that deviate from the ideal are common. Usually, measured APR values are lower than expected, and a number of mechanisms can be invoked to explain shortages in acid production. Indeed, almost all chemical processes have product recoveries of less than 100%. In electrowinning, an excess of acid is occasionally produced (i.e., APR > 2). Excess acid production is somewhat more difficult to explain than is deficient acid production, and in what follows an explanation for apparent excess acid generation is offered as a useful illustration of extending a simple physical model to accommodate real world results.

An actual electrowinning process is accurately represented in Figure 2.

The desired cathode process is the electrodeposition of metal (upper-left portion of Figure 2):

$$M^{2+}\ (aq) + e^- \rightarrow M(s)$$

M = some appropriate metal (e.g., Cu, Ag, Pd, etc.).

The desired anode process is the oxidation of H_2O (upper-right portion of Figure 2):

$$H_2O - 2e^- \rightarrow 2\ H^+(aq) + ½\ O_2(g)$$

An undesired cathode process is the reduction of the H_2O (lower-left portion of Figure 2):

$$2\ H_2O + 2\ e^- \rightarrow 2\ OH^-(aq) + H_2(g)$$

An undesired anode process is the oxidation of M^{2+} to M^{4+} (lower-right portion of Figure 2):

$$M^{2+}\ (aq) - 2e^- \rightarrow M^{4+}\ (aq)$$

In the rest of this discussion we will set the above-described electrowinning experiment for the passage a total of 2 mol of

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electrons. To enable a reasonably compact derivation, we will assume that the metal cation can only exist in the M^{2+}/M^{4+} oxidation states. We will also assume that M^{2+} is unhydrolyzed under the conditions of the experiment, but we will allow M^{4+} to be hydrolyzed to any degree. By hydrolysis we are referring to reactions of metal cations with water to yield metal oxides and acid (e.g., $M^{4+} + 2\ H_2O \rightarrow 4\ H^+ + MO_2$) [2]. Equations similar to those discussed herein can be derived for metal cations with different valence and hydrolysis profiles, but for this paper we will restrict the discussion to metal cations that exist only as unhydrolyzed M^{2+} ions and variably hydrolyzed M^{4+} ions. Finally, we will assume that the four electrochemical processes outlined above are the only ones which occur.

We define some variables as follows.
a = moles of M^{2+} reduced on the cathode
b = moles of OH^- produced at the cathode
c = moles of H^+ produced on the anode
d = moles of M^{2+} oxidized at the anode

As a total of 2 mol of electrons are passed, we also have the relationships:

$$2a + b = 2$$

$$c + 2d = 2$$

Note that the range of values that a and d can assume is between 0 and 1. The value of the APR will depend on the degree to which M^{2+} is oxidized to M^{4+} and upon the extent to which any M^{4+} formed is hydrolyzed. Note that APR values can be negative when net production of hydroxide occurs (i.e., when the extent of water reduction at the cathode exceeds the extent of water oxidation at the anode).

Explaining Excess-Acid Production

The case where a = 1 and d = 0 represents an ideal electrowinning process in which no by-products are formed on the anode or cathode. The case where a = 0 and d = 1 represents a process where we have total by-product formation on both the anode and cathode. The case where a = 1 and d = 1 represents a process wherein there is only by-product formation on the anode, but the cathode is behaving ideally. Finally, the case of a = 0 and d = 0 represents simply water being electrolyzed. In the case of water electrolysis (a = 0 and d = 0), we expect the APR to always equal zero as no actual electrowinning is occurring (i.e., there is no net acid production and there is no metal removal). Note that the equations derived later sometimes imply that the APR can have a value other than zero even though both a and d equal zero. This implication is an anomaly of the mathematics, as the appropriate equations always contain a term with an undefined quotient 0/0, which must be assumed to exactly offset all other defined terms to yield a final result of APR = 0. In all other cases, including equations with a and d equal to zero, but no defined terms, undefined quotients (0/0) are assumed to be equal to zero.

It is instructive to examine some limiting cases wherein M^{4+} is assumed to hydrolyze in a way that yields only one species. The APR values for limiting cases, such as those discussed above, can be calculated in a straightforward manner. Referring to the definitions above and taking n to be the degree of hydrolysis of M^{4+} (i.e., n equals the number of protons produced by hydrolysis reactions),

APR = (acid produced − base produced) ÷ (metal electrodeposited + metal ion precipitated)

$$\text{APR} = \frac{c - b + nd}{a+d} = \frac{2-2d-(2-2a) + nd}{a+d} = \frac{2a-2d+nd}{a+d}$$

for cases involving insoluble M^{4+} and

$$\text{APR} = \frac{c - b + nd}{a} = \frac{2-2d-(2-2a) + nd}{a} = \frac{2a-2d+nd}{a}$$

for cases involving soluble M^{4+}. For example, in the case wherein M^{4+} is completely unhydrolyzed and totally insoluble, the APR is equal to $(2a - 2d)/(a + d)$. Using similar logic, the expected APR values can be calculated for any number of defined limiting cases. Note that the APR values for a given limiting case are expressed as a function of a and d, and as a and d can take any value between 0 and 1, so too can the APR take on a range of values for any given case. APR equations and maximum/minimum APR limits for the limiting cases associated with the species shown in Figure 2 (i.e., I, II, and III) are listed below.

Figure 2, I(s), $M(OMs)_4(s)$:
M^{4+} Unhydrolyzed & Insoluble

$$\text{APR} = \frac{c-b}{a+d} = \frac{2-2d-(2-2a)}{a+d} = \frac{2(a-d)}{a+d}$$

a = 1 and d = 0: APR = 2 (Ideal)
a = 0 and d = 1: APR = −2
a = 1 and d = 1: APR = 0
a = 0 and d = 0: APR = 0 (by definition)

Figure 2, I(aq), $M(OMs)_4(aq)$:
M^{4+} Unhydrolyzed & Soluble

$$\text{APR} = \frac{c-b}{a} = \frac{2-2d-(2-2a)}{a} = \frac{2(a-d)}{a}$$

a = 1 and d = 0: APR = 2 (Ideal)
a = 0 and d = 1: APR = $-\infty$
a = 1 and d = 1: APR = 0
a = 0 and d = 0: APR = 0 (by definition)

Figure 2, II(s), $MO(OMs)_2(s)$:
M^{4+} half hydrolyzed & Insoluble

$$\text{APR} = \frac{c-b+2d}{a+d} = \frac{2a-2d+2d}{a+d} = \frac{2a}{a+d}$$

a = 1 and d = 0: APR = 2 (Ideal)
a = 0 and d = 1: APR = 0
a = 1 and d = 1: APR = 1
a = 0 and d = 0: APR = 0 (by definition)

Figure 2, II(aq), $MO(OMs)_2(aq)$:
M^{4+} half hydrolyzed & Soluble

$$\text{APR} = \frac{c-b+2d}{a} = \frac{2a-2d+2d}{a} = 2$$

$1 \geq a \geq 0$ and $1 \geq d > 0$: APR = 2
$1 \geq a > 0$ and $1 \geq d \geq 0$: APR = 2
a = 0 and d = 0: APR = 0 (by definition)

Figure 2, III(s), $MO_2(s)$:
M^{4+} fully hydrolyzed & Insoluble

$$\text{APR} = \frac{c-b+4d}{a+d} = \frac{2a-2d+4d}{a+d} = 2$$

$1 \geq a \geq 0$ and $1 \geq d > 0$: APR = 2
$1 \geq a > 0$ and $1 \geq d \geq 0$: APR = 2
$a = 0$ and $d = 0$: APR = 0 (by definition)

Figure 2, III(aq), $MO_2(aq)$:
M^{4+} fully hydrolyzed & Soluble

$$\text{APR} = \frac{c-b+4d}{a} = \frac{2a-2d+4d}{a} = \frac{2(a+d)}{a}$$

$a = 1$ and $d = 0$: APR = 2 (Ideal)
$a = 0$ and $d = 1$: APR = $+\infty$
$a = 1$ and $d = 1$: APR = 4
$a = 0$ and $d = 0$: APR = 0 (by definition)

The actual electrowinning process will be composed of some combination of all possible limiting cases. For instance, if we arbitrarily assume that only $M(OMs)_4(aq)$ and $MO_2(s)$ exist and that α is the extent of the $M(OMs)_4(aq)$ process and β is the extent of the $MO_2(s)$ process ($\alpha + \beta = 1$ as there must be one mole of total reaction extent), then using the derivations above,

$$\text{APR} = \alpha\frac{2(a-d)}{a} + 2\beta \; = \; \alpha\frac{2(a-d)}{a} + 2(1\text{-}\alpha)$$
$$= \; \alpha\frac{2(a-d)}{a} + \frac{2a(1-\alpha)}{a} = \frac{2a\alpha - 2d\alpha + 2a - 2a\alpha}{a}$$

$$\text{APR} = \frac{2a - 2d\alpha}{a} = \frac{2(a-\alpha d)}{a}$$

The limits for possible APR values from the equation above are $-\infty \leq \text{APR} \leq 2$:

$a = 1, d = 0$: APR = 2
$a = 1, d = 1$ and $\alpha = 0$: APR = 2
$a = 1, d = 1$ and $\alpha = 1$: APR = 0
$a = 0, d = 0$: APR = 0 (definition)
$a = 0, d = 1$ and $\alpha = 0$: APR = 0
$a = 0, d = 1$ and $\alpha = 1$: APR = $-\infty$

A great range of APR values can be explained with the above equation, but we know from real experiments that the APR value can exceed 2. Based on measured APR values greater than 2 the above equation is obviously inadequate [3]. In order to get an APR greater than 2, one must allow for the presence of soluble M^{4+} species that are more than half hydrolyzed. In the case of the model we are developing here there are two such species:

$$MO(OH)(OMs)(aq)$$

$$MO_2(aq)$$

If we assume that $MO_2(aq)$ does not exist to any significant extent, but we do allow for $M(OMs)_4(aq)$, $MO_2(s)$ and the soluble ¾-hydrolyzed species $MO(OH)(OMs)(aq)$ to be formed to extents α, β, and γ respectively ($\alpha + \beta + \gamma = 1$), then we get the following equation for the APR:

$$\text{APR} = \alpha\frac{2(a-d)}{a} + 2\beta + \gamma\frac{2a+d}{a} = \alpha\frac{2(a-d)}{a}$$
$$+ 2(1-\alpha-\gamma) + \gamma\frac{2a+d}{a}$$

$$\text{APR} = \alpha\frac{2(a-d)}{a} + 2 - 2\alpha - 2\gamma + \gamma\frac{2a+d}{a} = 2$$
$$+ \frac{2a\alpha - 2d\alpha - 2a\alpha - 2a\gamma + 2a\gamma + d\gamma}{a}$$

$$\text{APR} = 2 + \frac{d\gamma - 2d\alpha}{a} = 2 + \frac{d(\gamma - 2\alpha)}{a} = 2 + \frac{d}{a}(\gamma - 2\alpha)$$

The limits for possible APR values from the equation above are $-\infty \leq \text{APR} \leq +\infty$.

$a = 1, d = 0$: APR = 2
$a = 1, d = 1, \alpha = 0$ and $\gamma = 0$: APR = 2
$a = 1, d = 1, \alpha = 0$ and $\gamma = 1$: APR = 3
$a = 1, d = 1, \alpha = 1$ and $\gamma = 0$: APR = 0
$a = 0, d = 0$: APR = 0 (definition)
$a = 0, d = 1, \alpha = 0$ and $\gamma = 0$: APR = 2
$a = 0, d = 1, \alpha = 0$ and $\gamma = 1$: APR = $+\infty$
$a = 0, d = 1, \alpha = 1$ and $\gamma = 0$: APR = $-\infty$

This equation allows for an APR value greater than 2, but by limiting the equation to only a few possible by-products we have decreased our understanding of the process as a whole.

The General Equation

In what follows we will develop a completely general equation for the APR based on a linear combination of all possible limiting cases. Note that each term in this linear combination contains both an ideal (electrowinning) and a nonideal (M^{4+} by-product hydrolysis) contribution. Following the discussion of the linear combination scheme, a different derivation of the same general APR equation will be presented. This alternative derivation will employ a summation of the (total ideal) plus (total nonideal) contributions.

First we label the extent of each of the limiting cases:

α_{aq} = extent of $M(OMs)_4(aq)$ case
β_{aq} = extent of $M(OH)(OMs)_3(aq)$ case
γ_{aq} = extent of $MO(OMs)_2(aq)$ case
δ_{aq} = extent of $MO(OH)(OMs)(aq)$ case
ε_{aq} = extent of $MO_2(aq)$ case
α_s = extent of $M(OMs)_4(s)$ case
β_s = extent of $M(OH)(OMs)_3(s)$ case
γ_s = extent of $MO(OMs)_2(s)$ case
δ_s = extent of $MO(OH)(OMs)(s)$ case
ε_s = extent of $MO_2(s)$ case

Next we define some useful sums:

$\Psi_s = (\alpha_s + \beta_s + \gamma_s + \delta_s + \varepsilon_s)$ = extent of M^{4+} hydrolysis reactions producing insoluble species.

$\Psi_{aq} = (\alpha_{aq} + \beta_{aq} + \gamma_{aq} + \delta_{aq} + \varepsilon_{aq})$ = extent of M^{4+} hydrolysis reactions producing soluble species.

$\Omega_s = (2\varepsilon_s + \delta_s - \beta_s - 2\alpha_s)$ = molar acid excess produced by insoluble M^{4+} species.

$\Omega_{aq} = (2\varepsilon_{aq} + \delta_{aq} - \beta_{aq} - 2\alpha_{aq})$ = molar acid excess produced by soluble M^{4+} species.

We recognize that by definition the total extent of all reactions is 1:

$\alpha_{aq} + \beta_{aq} + \gamma_{aq} + \delta_{aq} + \varepsilon_{aq} + \alpha_s + \beta_s + \gamma_s + \delta_s + \varepsilon_s = 1$ = total extent of reactions.

Finally, we construct the following linear combination as a general equation for the APR.:

$$\text{APR} = \alpha_s(\text{APR for } \alpha_s) + \beta_s(\text{APR for } \beta_s) + \ldots$$

(sum of all terms)

$$\begin{aligned}\text{APR} = {} & \alpha_s \frac{2(a-d)}{a+d} + \beta_s \frac{2a-d}{a+d} + \gamma_s \frac{2a}{a+d} + \delta_s \frac{2a+d}{a+d} \\ & + 2\varepsilon_s + \alpha_{aq} \frac{2(a-d)}{a} + \beta_{aq} \frac{2a-d}{a} \\ & + 2\gamma_{aq} + \delta_{aq} \frac{2a+d}{a} + \varepsilon_{aq} \frac{2(a+d)}{a}\end{aligned}$$

Through rearrangement we get the following compact equation.

$$\text{APR} = 2\Psi_{aq} + \frac{2a}{a+d}\Psi_s + \frac{d}{a+d}\Omega_s + \frac{d}{a}\Omega_{aq}$$

APR Limits

One approach to the interpretation of undivided-cell electrowinning data involves examination of the limiting values possible for the APR as obtained from the general equation. The theoretical limits for a, d, Ψ_{aq}, Ψ_s, Ω_{aq}, Ω_s are

$0 \le a \le 1$, $0 \le d \le 1$, $0 \le \Psi_{aq} \le 1$, $0 \le \Psi_s \le 1$, $-2\Psi_{aq} \le \Omega_{aq} \le 2\Psi_{aq}$, $-2\Psi_s \le \Omega_s \le 2\Psi_s$

The general equation for the APR can be split into two parts as follows:

$$\text{APR} = \left[2\Psi_{aq} + \Psi_s \frac{2a}{a+d} + \Omega_s \frac{d}{a+d}\right] + \left[\Omega_{aq}\frac{d}{a}\right] = K_1 + K_2$$

With:

$$K_1 = 2\Psi_{aq} + \Psi_s \frac{2a}{a+d} + \Omega_s \frac{d}{a+d}$$

and

$$K_2 = \Omega_{aq}\frac{d}{a}$$

Based on the variable limits given above, the limiting values in the general APR equation are:

$a = 1, d = 0$: APR = 2
$a = 1, d = 1, \Psi_{aq} = 1, \Psi_s = 0$: $K_1 = 2, -2 < K_2 < 2$
$a = 1, d = 1, \Psi_{aq} = 0, \Psi_s = 1$: $0 < K_1 < 2, K_2 = 0$
$a = 0, d = 1, \Psi_{aq} = 1, \Psi_s = 0$: $K_1 = 2, -\infty < K_2 < \infty$
$a = 0, d = 1, \Psi_{aq} = 0, \Psi_s = 1$: $-2 < K_1 < 2, K_2 = 0$

In summary, the overall limits for the APR are as follows:

$$-2 \le 2\Psi_{aq} + \Psi_s \frac{2a}{a+d} + \Omega_s \frac{d}{a+d} \le 2,\ -\infty \le \Omega_{aq}\frac{d}{a} \le +\infty$$

It is obvious from a quick review of the APR limits that it is only through the $(d/a)\Omega_{aq}$ term that the APR can assume values greater than 2. Thus, any experiment that yields an APR value greater than 2 implies that $(d/a) > 0$, and that Ω_{aq} is positive.

Implications of an APR > 2

If the oxidation of M^{2+} to M^{4+} is possible, then the formation of M^{4+} ($d > 0$) during an undivided-cell electrowinning experiment is not surprising. In most cases the APR values for electrowinning experiments involving M^{2+} will be less than 2, but when APR values greater than 2 are found we can conclude that $d > 0$, $a > 0$, $(d/a) > 0$ and $\Omega_{aq} > 0$ ($\Omega_{aq} = 2\varepsilon_{aq} + \delta_{aq} - \beta_{aq} - 2\alpha_{aq}$). The inequality $\Omega_{aq} > 0$ requires that:

$$2\varepsilon_{aq} + \delta_{aq} > \beta_{aq} + 2\alpha_{aq}$$

Stated verbally, the above inequality requires that the portion of the APR which is greater than 2 derives exclusively from soluble M^{4+} species that are greater than one-half hydrolyzed at the pH used for the analysis of the free-acid content (e.g., pH = pK_a of the water-solvated proton for an aqueous pH titration). Remember that the value of the APR is dependent on the extent of completion of the electrowinning experiment (i.e., on the pH of the final solution). Unfortunately, further quantitative conclusions based on an APR > 2 are limited by the potential variability of the $\Psi_{aq} + \{2a/(a + d)\}\Psi_s + \{d/(a + d)\}\Omega_s$ portion of the general equation. One is unable to equate the magnitude of the APR in excess of 2 solely with the $(d/a)\Omega_{aq}$ term because changes in experimental conditions may be influencing the $\Psi_{aq} + \{2a/(a + d)\}\Psi_s + d/(a + d)\}\Omega_s$ portion of the equation as well. If one insures that $\Psi_{aq} + \{2a/(a + d)\}\Psi_s + \{d/(a + d)\}\Omega_s$ is essentially constant throughout a set of experiments, then relative conclusions concerning the nature of the hydrolyzed M^{4+} species produced can be made. Of particular value is the ability to rank different electrolytes with respect to the solubility of M^{4+} species.

Data for the Undivided-Cell Electrowinning of Metal Alkanesulfonates

Data collected from undivided-cell electrowinning experiments involving some metal alkanesulfonate salts is

Table 1. Undivided-Cell Electrowinning Data for Some Metal Alkanesulfonate Salts

Won Metal (Acid)[a]	APR[b]	% Completion[c]	Current Efficiency[d]
Palladium (MSA)	> 2	100%	57%
Silver (MSA)	1.9	97%	53%
Copper (PSA)	2	99%	79%
Tin (ESA)	1.9	99%	85%
Lead (MSA)	> 2	100%	130%[e]
Nickel (PSA)	0.6	29%	17%
Cadmium (PSA)	> 2	100%	46%
Iron (MSA)	1.0	15%	81%
Zinc (ESA)	1.6	92%	52%

[a] MSA = methanesulfonate, ESA = ethanesulfonate, PSA = propanesulfonate. [b] APR as defined in this paper. [c] The percentage of metal removed relative to what was present initially (+/– 0.5%). [d] The efficiency of current utilization relative to metal removal assuming an ideal process. [e] Values greater than 100% indicate a significant amount of non-ideal M^{4+} formation.

shown above in Table 1 (see references for experimental details) [3, 4].

For Pd(II), Pb(II), and Cd(II), the APR is greater than 2. This is consistent with the known chemistry of palladium and lead (i.e., Pd^{4+} and Pb^{4+} exist), but Cd^{2+} on the other hand is not known to form a higher-valent cation. The data for cadmium may have been influenced by the presence of finely colloidalcadmium metal in the product electrolysis solution. Such colloidal metal would have been picked up by the ICP/emission method that was used to analyze the solution for total metal content and thus would have caused an erroneous increase in the APR value for cadmium. This probable error points out the importance of rigorously filtering the final electrolysis solution prior to analysis for metal and acid content. APR values greater than 2 for the electrowinning of Pb^{2+} and Pd^{2+} in methanesulfonic acid are also consistent with field observations in the microelectronics plating industry that aqueous alkanesulfonic acid electrolytes have a high tendency to solubilize high valent metal cations. The semi-quantitative verification of such field observations with APR data is interesting.

Structure of Hydrolyzed M^{4+} Species

It should be mentioned that hydrolyzed metal cations such as the various M^{4+} species that have been referred to in this paper are known to adopt oligomeric structures [2]. This might imply that nonintegral levels of hydrolysis can exist for overall $(M^{4+})_n$ clusters, but it is not necessary to consider such states for the purposes of what we are discussing here. Whether or not a particular hydrolyzed M^{4+} species is part of a cluster is not important as long as we remember that we are examining the overall average hydrolysis state.

Another General Equation

A different approach involving a more standard (total ideal contribution) plus (total byproduct contribution) derivation of a general equation for APR was mentioned earlier and will be presented now. Remember that the APR is equal to the ratio of the number of moles of acid produced in the electrolysis solution to the number of moles of metal removed from the electrolysis solution (a = moles of metal removed, d = moles of M^{4+} produced, total extent of reaction = 2 moles of electron transfer). For every M^{4+} that is hydrolyzed, there is some net production of acid. A single proton is generated by each individual hydrolysis reaction. We can define a net acid production value (Ω_p) for M^{+4} hydrolysis as follows:

$$\Omega_p = \beta_{aq} + 2\gamma_{aq} + 3\delta_{aq} + 4\varepsilon_{aq} + \beta_s + 2\gamma_s + 3\delta_s + 4\varepsilon_s$$

This value is easily understood as 1 proton for a single hydrolysis times the mole fraction of M^{4+} that undergoes a single hydrolysis plus 2 protons for a double hydrolysis times the mole fraction of M^{4+} that undergoes a double hydrolysis, etc., until all contributions are summed. Using Ω_p as defined here and Ψ_s as defined previously, the following general equation is readily derived:

$$\text{APR} = (2a - 2d + d\Omega_p)/(a + d\Psi_s)$$

Take care not to confuse the $d\Omega_p$ and $d\Psi_s$ terms with differentials. These are simple products of d (moles of M^{4+} produced) with the other term.

By rearrangement of this equation we obtain:

$$\Omega_p = \{\text{APR}(a + d\Psi_s) - 2a + 2d\}/d$$

It is possible to measure APR, a, d and Ψ_s separately. A Redox titration can be used to analyze the electrowon solution for M^{2+} and M^{4+} content. The combined solids collected from the filtration operation along with scrapings from the anode surface can be combined in order to obtain their combined M^{4+} content. By combining the data from these two analyses one obtains d (the total amount of M^{4+} produced), Ψ_s (insoluble M^{4+} divided by d) and Ψ_{aq} (soluble M^{4+} divided by d). Finally, assuming the cathode electrodeposit is adherent, the value of a can be obtained by weighing the cathode before and after the experiment.

Conclusion

The use of mass-balance data for the optimization of electrowinning processes has long been understood; however, the full power of such data to shed light, at least in a semiquantitative way, on issues of metal-cation hydrolysis and speciation has been overlooked. In this paper, some approaches to maximizing the value of easily collected mass-balance data have been outlined, and a general equation relating the APR (acid-production ratio) to ion speciation has been derived in two ways. The first derivation provided an equation that is useful for getting the maximum amount of insight from a minimum amount of work. The second derivation provided an equation that is useful when a more time intensive total analysis of all reaction products is possible. These two equations are, of course, equivalent, but there does not appear to be any additional insight obtainable by setting the differently derived equations equal to one another and then rearranging. It is hoped that the methods described herein prove useful to those who teach electrochemistry and to those who collect undivided-cell electrowinning data.

References and Notes

1. A comprehensive SciFinder search revealed no prior art.
2. Baes, C. F.; Mesmer, R. E. *The Hydrolysis of Cations;* Krieger Publishing Company: Malabar, FL, 1986.

3. Gernon, M. D.; Martyak, N. M.; Nosowitz, M.; Smith, G. S. U.S. Patent 6*,187,169*, 2001.
4. Gernon, M. D.; Smith G. S.; Elkins J. Clean Effic. Process.: Electrochem. Technol. Synth., Sep., Recycle, Environ. Improv., Int. Forum, Electrolysis Chem. Ind. **1998**, 12, 252–285.