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1 Electrocrystallization and Solubility of Mercury in Alkaline Solution

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Abstract

The chemical thermodynamics of mercury in aqueous sodium hydroxide solution has been investigated through electrochemical polarisation and solubility experiments. A review of thermodynamic data allowed determination of the Hg/HgO electrode potential. Cyclic voltammetry revealed a complex anodic reaction beginning with aqueous dissolution of elemental mercury and subsequent electrocrystallization of mercuric oxide. Cathodic sweeps showed dual reduction reactions, attributed to the presence of aqueous mercury and mercuric oxide. The solubility and hence activity of elemental mercury in sodium hydroxide solution was determined, otherwise known as the Sechenov salt effect. Sodium hydroxide salted mercury out of solution.

Key words: Mercury, thermodynamics, electrochemical, electrocrystallization, solubility.

Introduction

Mercury is an ancient element notable for its liquid state at room temperature, hence ‘hydragyrum’, or liquid silver. Elemental mercury is characterised by its high volatility and hydrophobicity. The oxidised species is neurotoxic and exhibits bioaccumulative properties. These unfortunate confluences resulted in the death or eventual madness of convict labourers at the Almaden cinnabar mines, Minamata disease, and exposure resulting in long term sequelae for workers involved in industrial settings such as the Castner-Kellner process.¹ The widespread use of mercury for its alloying, catalytic and electrochemical properties²⁻³, has resulted in prolonged investigations to determine the behaviour of mercury in an environmental setting.⁴⁻⁶

Mercury is present as a trace contaminant in bauxite. The University of Queensland – Rio Tinto Bauxite and Alumina Technology Centre has analytical expertise in the determination of mercury in alkaline solution, and the development of novel mercury stabilising additives for the Bayer process.⁷⁻⁸ A recent study considered the chemical thermodynamics of mercury in the highly alkaline Bayer process,⁹ and here we determined the electrochemical kinetic behaviour of mercury in alkaline solution through electrochemical polarisation in synthetic solution. Thermodynamic data was reviewed, and the potential of the Hg/HgO electrode was calculated. In the Bayer process digestion stage, reducing conditions at elevated temperature result in the gaseous deportment of elemental mercury. Considering the development of Pitzer based models relevant to Bayer process conditions,¹⁰ we investigated the aqueous activity of elemental mercury in sodium hydroxide solution, known as the Sechenov salt effect.

Experimental

Cyclic Voltammetry

The electrochemical cell was a sealed, water jacketed glass vessel, with all experiments performed at 25 °C. Alkaline solution for all experiments was prepared by dissolving high purity NaOH pellets (Scharlau) in deionised water followed by PTFE membrane filtration through 0.45 µm pores. An HgCl₂ (Sigma-Aldrich) stock solution was prepared, with serial dilutions performed daily. Argon gas (99.5%) was used for deaeration. Cyclic voltammograms were carried out using a Volta Lab PGZ100 Potentiostat. The 2.0 mm diameter platinum rotating disk working electrode (surface area 0.314 cm²) was cleaned with 5% HCl then rinsed with deionised water before use and rotated at 1000 rpm during the experiment. A stable open circuit potential was established prior to initiating the potentiodynamic scan. The counter electrode was a 10 mm platinum wire (surface area 0.33 cm²). The Hg/HgO reference electrode (filled with 3.53 *m* NaOH solution) was manufactured by Koslow Scientific.

Solubility Cell

The solubility cell was a sealed, water jacketed glass apparatus (570 mL volume). Quick fit ports with inline stopcocks were utilised for sparging and purging solution. High purity liquid mercury was used to saturate the aqueous and subsequently gaseous phase. A non-flammable 5% H₂ 95% N₂ gas mixture was used to sparge the cell and provided a reducing atmosphere. Due to continuing evidence of oxidation, the cell solution was supplemented with 0.001 M NaBH₄ (Sigma-Aldrich). This low concentration of NaBH₄ will not have a significant effect on mercury solubility.¹¹

Equilibrium was achieved in 24 hours, with the cell contents mixed using a magnetic stirrer. Prior to sampling, the stirrer was turned off for a minimum of two hours. Sampling was performed by purging cell solution under the pressure of the 5% H₂ 95% N₂ gas. An initial aliquot was discarded to rinse the line, then a mass of solution was purged into a syringe and forced through a 0.45 µm PTFE filter into a 100 mL volumetric flask containing an oxidising HCl-BrCl solution. This solution was analysed using a Perkin Elmer FIMS 400 cold vapour atomic absorbance spectrometer, the validation and

89 methodology being previously described by Bansal, et al.⁷ Calibration standards were matrix matched
90 to the oxidising solution.

91

92 The Hg-HgO Alkaline System

93 Mercury in alkaline solution exists as the elemental or the mercuric species. In acidic solutions, the
94 dimeric mercurous species $\text{Hg}_2^{2+}(\text{aq})$ exhibits a narrow range of stability with regards to electrochemical
95 potential, prone to disproportionation into the elemental and mercuric species. Studies performed in
96 the early 19th century claimed use of a mercurous oxide electrode, but later spectroscopic examination
97 found these electrodes to consist of elemental mercury and mercuric oxide, $\text{HgO}_{(\text{s})}$.¹² In alkaline
98 solutions, the mercurous species is unknown. Sanemasa¹³ documented extremely rapid
99 disproportionation in 0.05 M NaOH solution.

100 At ambient temperatures, $\text{HgO}_{(\text{s})}$ exists as the red or yellow orthorhombic mineral montroydite, or
101 rarely as a metastable hexagonal variety with a structure analogous to cinnabar. Historically there has
102 been debate over whether the red and yellow species are in fact separate minerals, and numerous
103 studies have reported the solubilities of both varieties. It is common for the difference between the two
104 to be ascribed entirely to particle size,^{12, 14} and the most recent database indicated that the colour
105 change is due to defect growth¹⁵. Corti and Fernandez-Prini¹⁶ noted a 0.6 mV bias potential between
106 red and yellow Hg/HgO electrodes, which declined to 0.2 mV after alkaline digestion at 80 °C for four
107 days. This implies an ‘ageing’ process as encountered in the determination of zeta potential in
108 minerals, proposed to be due to establishment of a freely dissolving surface potential.¹⁷ Regardless, the
109 difference in solubility between the red and yellow varieties has been shown to fall within
110 experimental error, and no distinction is made between the two in regards to the results of this study.^{12,}
111 ¹⁸

112 Mercuric hydroxide is the predominant oxidised aqueous species in alkaline solution. The oxyanionic
113 species $\text{HHgO}_2^-(\text{aq})$, or equally the polyanionic species $\text{Hg}(\text{OH})_3^-(\text{aq})$ are known, however the

dissociation constant is speculative. Comprehensive literature reviews^{12, 18-19} rely on the dissociation constant of Garrett and Hirschler²⁰, which is a notional value assuming equal activity coefficients of OH^- and $\text{Hg}(\text{OH})_3^-$. As $\text{Hg}(\text{OH})_{2(\text{aq})}$ is a poorly soluble aqueous neutral, salting effects complicate the matter. $\text{Hg}(\text{OH})_{2(\text{aq})}$ is an extremely weak acid, but in highly alkaline solutions the formation of $\text{Hg}(\text{OH})_3^-$ is significant. There is an absence of data describing the formation of more complex hydroxide polyanions.

The soluble species are illustrated by way of a Pourbaix diagram in **Figure 1**, utilising the thermodynamic data discussed subsequently (**Tables 1-4**). The regressed solubility of elemental mercury in pure water (**Figure 5**) was used to determine the Gibbs free energy of aqueous elemental mercury, as non-ideal solute behaviour such as salting effects cannot be incorporated into a Pourbaix diagram. The diagram details aqueous elemental mercury in equilibrium with mercuric species at a 1 to 1 ratio, equivalent to the standard state. The solubility data determined in this study indicates a ratio of aqueous elemental to mercuric species on the order of 10^{-3} , and this is provided in the diagram. The equilibrium potential shifts anodically, as it must accommodate mass transfer law and the release of hydroxide to solution. By way of comparison, the equilibrium line for liquid elemental mercury is provided, which is unsurprisingly noble. It is seen that extremely alkaline conditions are required for the polyanionic species to be considered predominant. Note that the potentials provided in this Pourbaix diagram will not correlate to the Hg/HgO potential, as this is defined as solids in equilibrium.

Figure 1: Pourbaix diagram of soluble species in the alkaline mercury system at 25 °C.

An Hg/HgO reference electrode was utilised in this study, the electrode fill solution was the same as the test solution, eliminating the liquid junction potential. Equations 1 and 2 detail the reaction path, and it is noted that introduction of the polyanionic $\text{Hg(OH)}_3^-(\text{aq})$ species results in the same combined equilibrium constant. Therefore, all mercuric hydroxide species are eliminated from the combined equilibrium constant utilised in determining the Hg/HgO electrode potential.

The Gibbs energy of formation for $\text{HgO}_{(\text{s})}$ is well established, as per the review of Hepler and Olofsson¹⁹. These values for red and yellow $\text{HgO}_{(\text{s})}$ have been propagated widely through the review of Wagman, et al.²¹, initially determined through heat capacity derived entropy and electrochemical

data.²² Vanderzee, et al.²³ experimentally determined and reviewed the literature for red and yellow $\text{HgO}_{(s)}$, their data falling within 0.16 kJ mol^{-1} of the existing values, which they subsequently adopted. Later electrochemical evaluation and thermodynamic review of the Hg-HgO system was undertaken by Corti and Fernandez-Prini¹⁶, utilising a yellow Hg/HgO electrode in a multicomponent NaOH-KCl solution, with water activity determined through a binary mixing model. Longhi, et al.²⁴ investigated the Hg/HgO electrode in NaOH solution, assuming thermodynamic equality between red and yellow varieties. The value determined by Longhi et al. is substantially lower than previously, attributed by the author to improvements in cell separation. However, this should not affect calorimetric measurements, and this study adopts widely used value of the notionally thermodynamically stable red mercuric oxide detailed by Hepler and Olofsson¹⁹. Gibbs energy of formation of $\text{HgO}_{(s)}$ are listed in **Table 1**, with data of Bard, et al.²⁵ used for the remaining species.

The alkaline solubility of mercuric oxide was addressed by Hepler and Olofsson¹⁹, and reviewed thoroughly by Dirkse, et al.¹² and Powell, et al.¹⁸, with the latter two authors declining specification between red and yellow varieties. The review of Powell, et al.¹⁸ refined stability constant data, utilising specific interaction theory regressed to infinite dilution. Utilising the Gibbs energy data of Hepler and Olofsson¹⁹ for red $\text{HgO}_{(s)}$, Gibbs energies for $\text{Hg}(\text{OH})_{2(aq)}$ and $\text{Hg}(\text{OH})_3^-(aq)$ are determined (**Table 1**). The difference between the thorough reviews of Dirkse, et al.¹² and Powell, et al.¹⁸ is minimal, with the more recent study of Powell, et al.¹⁸ preferred for this study.

Table 1: ΔG° formation of $\text{HgO}_{(s)}$, $\text{Hg}(\text{OH})_{2(aq)}$ and $\text{Hg}(\text{OH})_3^-(aq)$. (a) Hepler and Olofsson¹⁹, (b) Longhi, et al.²⁴, (c) Corti and Fernandez-Prini¹⁶, (d) Dirkse, et al.¹², (e) Powell, et al.¹⁸.

$\text{HgO}_{(s)}$ (kJ mol^{-1})	-58.555 _{red (a)}	-58.450 _{yel (a)}	-58.238 _(b)	-58.476 _{yel (c)}
$\text{Hg}(\text{OH})_{2(aq)}$ (kJ mol^{-1})	-274.50 _(a)	-275.07 _(d)	-275.07 _(e)	
$\text{Hg}(\text{OH})_3^-(aq)$ (kJ mol^{-1})	-427.20 _(a)	-427.47 _(d)	-427.74 _(e)	

Further refinement requires determination of hydroxide activity and water activity, while $\text{HgO}_{(s)}$ and $\text{Hg}_{(l)}$ are assumed ideal. Water activity in NaOH solution is well established, and this study utilises the

regressed data supplied by Nickell, et al.²⁶, while a Pitzer derived mean activity coefficient sourced from Zemaitis, et al.²⁷ is utilised for hydroxide. The data and resulting pH of the experimental conditions is listed in **Table 2**. In 4 *m* NaOH solution an Hg/HgO potential relative to the standard hydrogen electrode (SHE) of 62.43 mV is predicted. Under the same conditions Longhi, et al.²⁴ experimentally determined a result of 57.5 mV. However, this necessitated the use of a calomel electrode attached to an equitransferent, double junctioned, saturated potassium chloride, caesium chloride (11 *m*) salt bridge. The author assumed a liquid junction potential maximum of 1.0 mV, with the difference to a theoretical value attributed to a single ion activity coefficient. As the liquid junction potential cannot be rigorously determined in concentrated solution, and single ion activity coefficients are subject to controversy, we adopt the mean activity coefficient.

Table 2: Activity of hydroxide, water and resulting pH in 3.53 m NaOH solution.

NaOH mol kg ⁻¹	OH ⁻ act. co-eff.	OH ⁻ act.	H ₂ O act.	pH
3.53	0.844	2.982	0.846	14.54

Platinum mercury amalgams and compounds are documented, with PtHg₄ and PtHg₂ the thermodynamically stable compounds at ambient temperature. Equilibrium may be reached slowly, over a period of days.²⁸ Claims have been made regarding a variety of platinum mercury compounds, and complex underpotential deposition behaviour has been clearly demonstrated in acidic media.²⁹ However, the species involved are controversial and thermodynamic data is lacking. Robbins and Enke³⁰ confirmed the existence of PtHg₄ through x-ray diffraction, and determined potential under standard conditions (E°) of +87 mV at 25 °C through a modified calomel cell, resulting in a Gibbs energy of formation of -34 kJ mol⁻¹. Jangg³¹ determined the ΔG° of PtHg₄ and PtHg₂ to be -60.2 and -33.1 kJ mol⁻¹ respectively, determined through extrapolation of high temperature vapour pressure measurements. This data is not preferred due to the large extrapolation to ambient. Thermodynamic data for amalgamation is necessarily limited to mixing, which is complicated by the determination of composition, and a lack of accurate data at ambient temperature. However, solubility of mercury in platinum is such that a mercury platinum solid solution is not visible on binary phase diagrams at ambient temperatures.^{28, 32}

Table 3 lists the resulting standard potentials (E°) and formal potentials (E_h) relevant to our experimental conditions of 3.53 *m* NaOH solution. Standard conditions are of course 1 *m* of ideal solute and referenced to SHE by definition. In addition all potentials have been corrected from atm to bar as per IUPAC. The formal potentials utilise the activities detailed in **Table 2**.

Table 4 lists the activity of $\text{Hg}(\text{OH})_{2(\text{aq})}$ and $\text{Hg}(\text{OH})_{3(\text{aq})}^-$ species in HgO saturated 3.53 *m* NaOH solution, with the data of Powell, et al.¹⁸ utilised for the dissolved mercuric species. The activity coefficient of dissolved mercuric species is assumed to be unity, which results in a close correlation with solubility determined by Garrett and Hirschler²⁰ of red $\text{HgO}_{(\text{s})}$. These authors determined solubilities of 2.94×10^{-4} and 2.97×10^{-4} *m* in 2.9 and 4.0 *m* $\text{NaOH}_{(\text{aq})}$ respectively.

Table 3: Reduction potentials of reactions relevant to cyclic voltammetry experiments.

	Alkaline E° (mV, bar)	E_h 3.53 <i>m</i> NaOH (mV, bar)
$\text{HgO}_{(\text{s})} + \text{H}_2\text{O} + 2\text{e}^- = \text{Hg}_{(\text{l})} + 2\text{OH}^-$	97.53	67.31
$4\text{HgO} + \text{Pt} + 4\text{H}_2\text{O} + 8\text{e}^- = \text{PtHg}_4 + 8\text{OH}^-$	141.58	111.36
$\text{PtO} + \text{H}_2\text{O} + 2\text{e}^- = \text{Pt} + 2\text{OH}^-$	151.95	121.73
$\text{PtO}_2 + \text{H}_2\text{O} + 2\text{e}^- = \text{PtO} + 2\text{OH}^-$	216.98	186.76

Table 4: Theoretical solubility of HgO in 3.53 *m* NaOH.

	$\text{Hg}(\text{OH})_{2(\text{aq})}$ activity (<i>m</i>)	$\text{Hg}(\text{OH})_{3(\text{aq})}^-$ activity (<i>m</i>)	Total $\text{Hg}(\text{II})_{(\text{aq})}$ activity (<i>m</i>)
HgO saturated 3.53 <i>m</i> NaOH	2.03×10^{-4}	9.37×10^{-5}	2.97×10^{-4}

Electrochemical Polarisation

Cyclic voltammetry was performed in deaerated 3.53 *m* NaOH solution saturated with $\text{HgO}_{(\text{s})}$ at 25°C.

The results of a 5 mV s⁻¹ scan are displayed in

208

209 **Figure 2** and the Tafel plot of the first cycle is displayed in **Figure 3**. The scan was initiated in the
210 cathodic region at -232 mV vs SHE and the potential was then increased in the anodic direction until
211 360 mV when the direction was reversed. A substantial anodic peak is observed at 103 mV with a
212 secondary peak at 134 mV. On the reverse scan, a cathodic peak is apparent at 36 mV, followed by an
213 extended relaxation towards a diffusion limited current. With subsequent scans, the current increases
214 significantly. As the current is transport limited and negligible at the end potentials, it is unlikely either
215 accumulation of neutral $\text{Hg}(\text{OH})_{2(\text{aq})}$ species in the boundary layer or extended sweep time on later
216 scans are contributory factors. Oxidative electrocrystallization is discussed subsequently, and it is
217 likely that this process conditions the surface of the electrode, allowing the formation of a more
218 comprehensive multilayer on the second and third scan cycles.

Figure 2: 5 mV s⁻¹ scan rate in HgO saturated 3.53 m NaOH solution.

Detail about the reaction pathway is revealed by considering the apparent Tafel regimes in **Figure 2**. The cathodic Tafel slope is unremarkable, with a gradient of -15.8 mV per decade implying a transfer coefficient of two for a two electron reduction of unknown mechanism. The primary anodic peak exhibits two distinct Tafel regions. The first anodic slope of 26.4 mV per decade implies a charge transfer coefficient of one for a two electron oxidation. The second anodic slope is a result of this reaction being surpassed by a reaction with a slope of 3.0 mV per decade. The second anodic peak generates a third Tafel slope that is convoluted by the first peak. The third Tafel slope is 25.9 mV per decade. The equilibrium potential from extrapolating the cathodic Tafel slope and the first anodic slope to their intercept is 64 mV, with the apparent exchange current density for the reaction being 0.48 A m⁻².

Figure 3: Tafel plot of first 5 mV s⁻¹ cycle, Hg/HgO E_n marked on potential axis.

The first anodic slope apparent at 80 to 95 mV is assumed a dissolution current due to the oxidation of mercury to form soluble mercuric hydroxide species. The second anodic slope apparent between 98-102 mV is 3.0 mV per decade, indicating kinetics that are not characteristic of the ionic discharge limiting Butler-Volmer equation. This is a result of oxidative electrocrystallization, which has been investigated thoroughly in systems characterised by poor solubility and the formation of thin passivating films. Mercury and amalgam electrodes are commonly employed to provide a homogenous surface equivalent to a perfect crystal plane, and previous studies include calomel, mercurous oxalate and cadmium hydroxide systems³³. The Avrami equation is employed to model the transient at constant potential, derived as a time invariant Poisson distribution in order to calculate the probability of overlapping crystal geometry and hence fractional surface coverage, providing the current density. The crystal growth rate is constant, but the nucleation rate may be progressive or

instantaneous.³⁴ The key understanding is that as the equation is time invariant, requiring a constant crystal growth rate, the rate limiting step must be the incorporation of adsorbed or aqueous ions into the crystal lattice, as the growth sites are subject to varying diffusion fields as crystallisation occurs.³⁵ The facile kinetics implies a significant alteration to the activation energy of ionic desolvation and discharge, or an excess of adsorbed ions. In 10 M NaOH, Armstrong, et al.³⁶ demonstrated an 18% surface coverage of adsorbed hydroxide at the monolayer potential, discussed subsequently.

Armstrong, et al.³⁷ utilised a dropping mercury electrode in 5 M NaOH to evaluate anodic electrocrystallization of mercuric oxide. Constant potential transient peaks, corresponding to separate equilibrium potentials for crystallisation of a monolayer and a multilayer, were found at overpotentials +15 mV and +24 mV relative to the Hg/HgO electrode, the equilibrium of which is dissolution of $\text{Hg}(\text{OH})_2(\text{aq})$. Crystallisation resulted in $\text{HgO}_{(\text{s})}$ crystals aligned to the surface along the 010 plane, with multilayer growth modelled as right circular cones, characteristic of Frank Read sources. Our experimental results demonstrate a crystallisation potential of +22.0 mV relative to Hg-HgO equilibrium. It is perplexing that the monolayer potential is not observed in this study, as assuming a square packing density and a perfectly smooth surface, 57 layers are oxidised in the first peak. It is noted that while the formation of a monolayer results in a drop in capacitance, a faradaic pseudo-capacitance follows, indicative of continuing dissolution with the monolayer functioning as an ionic conductor,³⁶ and this dual reaction may have obscured the transient. The composite rate constant for multilayer growth orthogonal to the electrode is potential driven, with Armstrong, et al.³⁷ demonstrating a potential dependence of 3.5 mV per decade. Barradas, et al.³⁸ demonstrated 3.1 mV per decade using data corrected for ohmic overpotential, in 5 M KOH solution. This is in close agreement with our result of 3.0 mV per decade. Similar gradients present in the anodic crystallisation of cadmium hydroxide, calomel and cinnabar.³⁹

The source of the second oxidation peak is difficult to interpret. This peak presumably includes the layers remaining in contact with platinum, and integration yields 14 layers. It is noted that the first cathodic peak yields 22 layers, however, there are geometric difficulties in determining its area. If the anodic Tafel slope of 25.9 mV per decade is assumed accurate, it yields an equilibrium potential 8.8

271 mV positive to Hg/HgO which is substantially less than would be expected if it were PtHg₄. However,
272 if this is a case of underpotential deposition, it is difficult to ascertain peak separation on the cathodic
273 sweep, and the cathodic Tafel slope may not represent the relevant redox couple. The third anodic
274 Tafel slope generated by the secondary anodic peak is of a similar gradient to freely dissolving
275 mercury, however, by the second peak it is sufficiently far from equilibrium that a more acute slope is
276 expected.

277 Through constant potential pulses, Barradas, et al.³⁸ detailed a discontinuity in the potential vs log
278 current slope, from 3.0 to 30 ± 5 mV per decade with increasing overpotential, without physical
279 explanation. Milchev and Vassileva⁴⁰ detailed similar discontinuities in the log nucleation rate at high
280 overpotentials, due to discrete changes in the critical nucleation energy, which is a function of the
281 number of adatoms. HgO electrocrystallization exhibits a progressive nucleation, and for this to be a
282 causative mechanism, it implies growth of the multilayer in its entirety is nucleation and not crystal
283 growth limited. Whatever the cause of the discontinuity, our slope of 25.9 mV per decade is of a
284 similar value. The experiment of Barradas, et al.³⁸ was conducted using a dropping mercury electrode,
285 without the involvement of platinum.

286 The cathodic sweep is characterised by a sharply defined peak, abruptly transitioning to a broad
287 reduction band. As the proportion of current related to HgO crystallisation increases on the second and
288 third cycles, the following cathodic sweep results in an increase of the reduction band, such that the
289 peak is obscured.

Figure 4: 100 mV s⁻¹ scan rate 3.53 m NaOH solution saturated with respect to HgO_(s).

Figure 4 details the results of a 100 mV s⁻¹ scan, the first cycle of which is similar to 5 mV s⁻¹, with the secondary anodic peak heavily distorted. The subsequent anodic cycles exhibit complex behaviour. A loop is presented in the secondary anodic peak, and compared to the usual declining transient, it is characterised initially by a reversal in sign of the rate of potential change. Equation 3 presents the output voltage (e_o) of the control amplifier in a potentiostat, which is applied to the counter electrode.⁴¹ The remaining symbols are input voltage (e_i), resistance of the solution and interface (R_{sol}), while R_2 is a constant.

$$e_o = -e_i \left(\frac{R_{sol}}{R_2} \right) \quad (3)$$

It is seen that a fall in interfacial resistance results in a reduction of the magnitude of applied potential. If at very high scan rates the op amp is unable to compensate immediately, the secondary peak will present as a loop. This requires instability of the HgO layer, which has been observed in the rupture and repair of dropping mercury electrodes in alkaline solution.⁴² It may be envisaged that the kinetics and morphology of growth occurring in the fractured layer is altered in comparison to the freely

growing surface. In the study of Pieterse, et al.⁴², it is noticeable that fitting of these periodic, post-rupture growth cycles to the Avrami equation demonstrated instantaneous nucleation. This implies that the secondary anodic peak is associated with film rupture. This behaviour is not observed in potentiostatic pulses of short duration, i.e. less than 200 ms.³⁷

Nevertheless, the high scan rate does result in almost the entirety of the current being due to HgO crystallisation. On the subsequent cathodic scans, the cathodic band is replaced with a shallow peak, indicating that the reduction band is associated with the kinetically slow reduction of HgO pyramids. Similar behaviour involving multiple layer peaks is observed in the alkaline cadmium amalgam system⁴³ and the acidic mercurous oxalate system⁴⁴. The initial cathodic peak is presumably associated with reduction of aqueous mercury.

Sechenov Salt Effect

In addition to the electrochemical study of the sparingly soluble oxidised species in alkaline solution, the varying solubility of hydrophobic aqueous elemental mercury in alkaline NaOH solution of increasing concentration was investigated. This change in solubility in the presence of an electrolytic co-solute is known as the Sechenov salt effect.

As a volatile hydrophobic solute, the solubility of gaseous elemental mercury is presented as Henry's constant, a measure of gas-aqueous phase partitioning. Solvation of gaseous elemental mercury has the thermodynamic characteristics typical of hydrophobic hydration, a strongly negative enthalpy and entropy combined with a large and positive Gibbs free energy, thereby being an entropy driven process.⁴⁵ As a neutral solute rarely possesses a dipole moment of sufficient magnitude in comparison to water, hydrophobic hydration results in water structuring itself around the solute. The exothermic character of solvation is primarily due to the formation of hydrogen bonds, and the entropy cost due to structuring of the solvation shell. Therefore, the thermodynamics of solvation are a function of the stronger interaction of water with itself than with the hydrophobic solute. This study is focused on

solution chemistry, and presents the thermodynamic data as dissolution of liquid mercury, which is assumed a pure substance.

The change in solubility of a hydrophobic solute with increasing salt concentration is known as the Sechenov salt effect, the relationship empirically described with the Sechenov equation (Equation 4), where c is salt concentration in units of choice, m_2^0 refers to the solubility of the hydrophobic solute in pure water and m_2 in salt solution. If the solubility of the hydrophobic solute in salt solution decreases, the effect is referred to as 'salting out'. Likewise, an increase in solubility is 'salting in'. A hydrophobic solute is effectively at infinite dilution, and in pure water it is considered ideal. The equation has a fundamental basis in as much as the excess Gibbs energy may be expressed as a linear function of concentration (Equation 5). In practice, the linear response for many solutes is observed to high salt concentrations.⁴⁶

$$\log\left(\frac{m_2^0}{m_2}\right) = k_s c \quad (4)$$

$$\frac{(u_{2(aq\ salt)} - u_{2(aq)}^0)}{RT} = \ln\left(\frac{m_2^0}{m_2}\right) = \ln \gamma^h \quad (5)$$

The question arises as to what is the cause of the change in activity of a non-electrolyte in an electrolyte solution. The activity of electrolytes with increasing concentration has been widely explored, the electrostatic 'screening', and therefore contribution to electrochemical potential, famously modelled in the continuum Debye-Hückel equation. However, such an effect does not apply to a neutral species.

Broadly speaking, high charge density ions encourage salting out, while low charge density ions encourage salting in. These effects were noted in the 19th century as the Hofmeister series, an empirical but loosely defined ranking of ions in their ability to salt proteins. The implication was that an electrolytic co-solute effects the local hydration of a non-polar solute, leading Debye and McAulay⁴⁷ to model salting out as a function of the macroscopic dielectric decrement upon addition of a non-electrolyte to water. For salting in, this model of hydrophobic solvation requires a dielectric increment, which is a rare occurrence. Salting in implies an increased affinity of the neutral species with the

solvent, leading Bockris, et al.⁴⁸ to develop a model based on the work of polarising a hydrophobic solute in the field of an ion. Attractive London dispersion forces between the neutral and ionic species are a function of polarisability, as the neutral species cancels the local electric field somewhat, reducing the dipole mediated interaction of water with itself. The electrostrictive effect of a dissolved salt is used for the internal pressure model,⁴⁹ and a variety of interaction potentials are used for a reference solute in scaled particle theory.⁵⁰ Recently, molecular dynamics simulations, utilising ions of constant radius but varying charge density, have demonstrated that salting out is an amplification of the entropy driven hydrophobic effect. The strong ion-water interaction of high charge density ions results in exclusion of ions from the region surrounding the hydrophobe, a subsequent local increase in water density and therefore a decrease of configurational entropy. This results in a greater entropic gain from a reduction in solubility, equivalent to an increase in activity of the hydrophobic solute. Salting in is a result of specific adsorption of the ion to the hydrophobic solute, effectively functioning as a surfactant.⁵¹⁻⁵²

The solubility of elemental mercury in pure water has been addressed by a small number studies, of which the most comprehensive review is that of Clever, et al.⁵³. The salting behaviour of mercury has been addressed in a select few studies, and the authors of this work are unaware of any evaluation of the salting behaviour of mercury in dissolved sodium hydroxide.

Solubility of Elemental Mercury in NaOH Solution

Figure 5 illustrates the solubility of mercury in pure water and NaOH_(aq). Mercury is salted out. The change in gradient of solubility with increasing concentration is indicative of the changing solution character. The solubility data is consistent with that provided in the review of Clever, et al.⁵³, closer to the lower values of Glew and Hames¹¹, who also utilised a reducing agent. The solubility values of Sanemasa⁵⁴ trend higher, however no reductant was used.

Figure 5: Solubility of mercury in pure water and sodium hydroxide solution.

Figure 6 graphs the Gibbs energy of phase change from pure water. A linear regression of the solubility data along the temperature axis was utilised, the results derived using the Van't Hoff equation. Notably the enthalpy of solution is positive, a reflection of bond breaking from the liquid mercury bulk.

Figure 6: Thermodynamics functions of aqueous phase change from pure water.

The work of aqueous phase change is the excess Gibbs energy, proportional to the activity coefficient, referenced to pure water. Therefore, in the initial state of work – mercury dissolved in pure water – the work of forming the hydrophobic cavity and coupling elemental mercury to the surrounding water molecules has already been performed. The work of phase change is the work of maintaining this mercury filled cavity in the presence of electrolytic co-solutes, and is intimately related to the solvation layers surrounding mercury.

The Gibbs energy of phase change to 0.49 *m* solution has a large entropic opposition with a corresponding exothermic, enthalpic contribution. This is consistent with salting out amplifying the hydrophobic effect, an increased entropic cost for the hydrophobe to be present in the dense, ion excluded water. At 0.96 *m* the entropy and enthalpic terms change sign, and at 1.85 *m* there is a large entropic contribution and a corresponding enthalpic opposition. The entropic contribution to phase change indicates that mercury is destructuring water. This is likely due to the gradient of local ionic concentration from the bulk to the solvation layers surrounding a hydrophobic species. At very high bulk concentration, ions will further enter the hydrophobic solvation layers. Ionic solvation shells are highly ordered in the first solvation shell, and form complex assemblages in the outer layers. Alkali cations are capable of forming clathrate structures,⁵⁵ while high concentrations of hydroxide ions results in the breakdown and interpenetration of the outer ionic solvation layers.⁵⁶ The presence of a hydrophobic solute in these complex water structures results in a net destructuring of water. The endothermicity of phase change may be thought of as the energy cost of breaking the hydrogen bonds of these structures.

Figure 7: Sechenov plot for elemental mercury in NaOH.

Figure 7 plots the Sechenov equation, with the gradient equal to the Sechenov constant. The Sechenov plot in **Figure 7** demonstrates a loss of linearity. This is not necessarily surprising, as non-linearity is demonstrated at comparable concentrations in the case of non-polar gases,⁵⁷ particularly when aggressive salting out occurs.

Table 5 demonstrates that this is the case for NaOH, with comparable salting behaviour only observed in the divalent Na_2SO_4 .

The individual Sechenov constants, as may be visualised by the data points in **Figure 7**, indicate increasing salting out with temperature in 0.49 molal solution, and decreasing salting out with temperature in 1.85 molal solution. There is constancy at 0.96 molal. This results in an inflection point as a function of temperature. The inversion reflects the transition of salting out from an entropy driven process to an enthalpy driven process with increasing concentration. In this manner, solution temperature aids mercury dissolution at low concentration, and opposes it at higher concentration. The effect is clearly visible upon examination of the solubility gradients in **Figure 5**, which demonstrate the reason for the initially exponential Sechenov response at 25 °C. The physicochemical processes

are difficult to elucidate. However, in the limiting case of static ionic concentration and increasing concentration of polarisable neutral co-solutes, solubility minima and maxima are observed⁵¹.

The internal pressure model was utilised for NaOH data valid at 25 °C,⁵⁸ and the resulting Sechenov constant of 0.140 is reasonably consistent with the individual Sechenov constant of 0.128 at 25 °C in 0.49 molal solution. However, the correlation was poor at higher concentrations, and it was demonstrated by Sanemsa, et al.⁵⁹ that there was generally poor correlation with a variety of salts which demonstrated an ideal, linear Sechenov gradient for elemental mercury.

Table 5: Sechenov constants provided by this study (a), Glew and Hames⁶⁰ (b) and Sanemsa, et al.⁵⁹ (c). (a) and (b) provided on molal basis for solute and electrolyte, (c) molarity basis for solute and electrolyte.

°C	NaOH	NaCl	NaF	NaCl	NaBr	NaClO ₄	NaNO ₃	NaSCN	Na ₂ SO ₄
Source	a	b	c	c	c	c	c	c	c
25	0.258	0.042	0.157	0.078	0.0173	0.117	0.061	-0.035	0.308
30	0.213	0.031							
35	0.180	0.022							
40	0.154	0.014							

Table 5 details Sechenov constants determined in this study, the study of Sanemsa, et al.⁵⁹ and the individual 6 molal NaCl Sechenov constant determined by Glew and Hames⁶⁰. The Sechenov constants indicate that sodium hydroxide is very effective at salting out mercury. This is surprising, as neither sodium nor hydroxide are very high charge density ions. This unpredictable behaviour is typical of specific ion effects exhibited in the Sechenov salt effect. Na₂SO₄ was a similarly effective salting agent, due to its divalent state. Thiocyanate demonstrates its chaotropic character as it salts mercury in. The influence of specific ion effects is demonstrable in the halide group, which is not a strict function of charge density. As sodium is a common cation in these systems, it may be assumed that the pronounced salting out of elemental mercury is predominantly due to hydroxide.

Conclusion

The chemical thermodynamics of mercury in alkaline solution was analysed through electrochemical polarisation and solubility investigations. The oxidation of mercury was characterised initially by dissolution of aqueous mercuric hydroxide species. With increasing potential the formation of an anodically electrocrystallized HgO multilayer was demonstrated. The formation of this layer is characterised by facile kinetics. Cathodic sweeps demonstrated dual peaks, associated with the reduction of aqueous mercury and the HgO layer. The solubility of elemental mercury was investigated in pure water and in NaOH solution. NaOH demonstrated a substantial Sechenov salt effect on mercury, similar only to the divalent sulfate anion. Literature review demonstrated that this is attributable to hydroxide.

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Abstract Graphic

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