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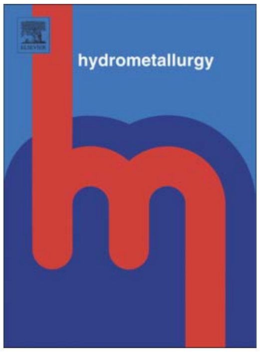
Navarro, M., May, P.M., Hefter, G. and Königsberger, E. (2014) Solubility of CuO(s) in highly alkaline solutions. Hydrometallurgy, 147-148. pp. 68-72.



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PII: S0304-386X(14)00098-X
DOI: doi: 10.1016/j.hydromet.2014.04.018
Reference: HYDROM 3884

To appear in: *Hydrometallurgy*

Received date: 12 February 2014
Revised date: 21 April 2014
Accepted date: 23 April 2014

Please cite this article as: Navarro, Maribel, May, Peter M., Hefter, Glenn, Königsberger, Erich, Solubility of CuO(s) in highly alkaline solutions, *Hydrometallurgy* (2014), doi: 10.1016/j.hydromet.2014.04.018

Solubility of CuO(s) in highly alkaline solutions

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Abstract

The solubility of tenorite, CuO(s), has been measured at 25 °C and 60 °C as a function of total hydroxide concentration, $[\mathrm{OH}^-]_\mathrm{T}$, at constant ionic strength (I = 5 or 6 mol kg^{-1}) in Li(OH,ClO$_4$)(aq) and Na(OH,ClO$_4$)(aq) media. Additional measurements were also made in highly concentrated (≥ 6 mol kg^{-1}) NaOH(aq) and KOH(aq). The solubility (S) of CuO(s), measured as the total concentration of dissolved Cu(II) by atomic absorption spectroscopy, decreased at approximately constant $[\mathrm{OH}^-]_\mathrm{T}$ in the order LiOH >> NaOH > KOH and increased with temperature and $[\mathrm{OH}^-]_\mathrm{T}$ in all media. Plots of log S against log $[\mathrm{OH}^-]_\mathrm{T}$ were linear with a slope of ~2.0, indicating, consistent with UV-Vis spectra, that the only significant Cu(II) species in solution was $\mathrm{Cu(OH)}_4^{2-}$(aq) under all conditions studied. Detailed analysis indicates that previous studies overestimated S because of the presence of fine particles of CuO(s). Using equilibrium constants and SIT parameters derived from the present experimental data, the solubility of CuO(s) could be described with good precision up to the highest hydroxide concentrations investigated in all media.

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Keywords: Copper(II) oxide, tenorite, solubility, lithium, sodium, potassium, hydroxide, modelling, thermodynamics.

1. Introduction

The Bayer process is exploited worldwide for the extraction of alumina from bauxite ores. Despite the maturity of this technology, some 120 years after its invention there are still many aspects of the process that are not well understood. An example is the redox chemistry of trace elements, which can depend strongly on the highly caustic Bayer process liquors (Zydorczak et al., 2012). Given the mineralogical complexity of typical feedstock ores, numerous redox-active elements invariably enter the process stream, even if only in trace amounts. Copper is one such element. While the amounts of Cu occurring in bauxite ores are typically low (<100 ppm) (Ayorinde, 2011), the cyclical nature of the Bayer process means that its concentration can build up over time. This is particularly important because Cu(II) catalyses the ‘wet’ oxidation (Tardio et al., 2005) of the (under some circumstances undesirable) organic substances that are always present in real Bayer process solutions. Ultimately, the concentration of dissolved Cu in Bayer process solutions will be determined, as for most trace elements, by the solubility of its oxide(s) or (oxy)hydroxide(s) and the strength of its complexation by the hydroxide ion (Baes and Mesmer, 1976). These two factors generally overwhelm any other effects (such as complexation by organic substances) in strongly alkaline solutions. It is therefore of some importance for improving our understanding of Bayer liquor chemistry to have reliable information on both the solubility of Cu(II) and the nature and strength of its hydroxo complexes in very concentrated caustic solutions.

Rather few experimental data for the solubility of copper(II) oxide in caustic solutions have been reported (Müller, 1923; McDowell and Johnston, 1936; Akhmetov et al., 1967). Baes and Mesmer (1976) have based their evaluation on the data of McDowell and Johnston (1936) who measured the solubility of CuO(s) in KOH(aq) from 0.04 to 8.38 mol kg^{-1} and in 2.2, 3.2 and 4.2 mol kg^{-1} NaOH(aq) at 25 ^{o}C. Akhmetov et al. (1967) determined CuO(s) solubilities in 1 to 10 mol L^{-1} NaOH(aq) from (25 to 200) ^{o}C. The solubility data obtained by some of these workers (McDowell and Johnston, 1936; Akhmetov et al., 1967) have been used by Plyasunova et al. (1997) to estimate thermodynamic parameters for the formation of the copper(II)-hydroxo complexes, $Cu(OH)_3^-$(aq) and $Cu(OH)_4^{2-}$(aq), using the Brønsted-Guggenheim-Scatchard Specific Ion Interaction Theory (SIT) (Grenthe at al., 1997). The stability of $Cu(OH)_4^{2-}$(aq) has been confirmed at different temperatures (20, 50 and 70 ^{o}C) using polarography and spectrophotometry (Norkus and Vaskellis, 1994). However, the existence of even higher order Cu(II)–OH$^-$ complexes remains an open question: the only solubility study of CuO(s) in highly concentrated NaOH(aq) was published 90 years ago (Müller, 1923) and a comparison with the other data sets available (McDowell and Johnston, 1936; Akhmetov et al., 1967) reveals a number of discrepancies. Furthermore, none of these older studies (Müller, 1923; McDowell and Johnston, 1936; Akhmetov et al., 1967) were carried out at constant *I* and to some extent thus reflect variations in activity coefficients.

In the present study, the solubility of tenorite, CuO(s), has been determined at 25 °C and 60 °C in Li(OH,ClO$_4$)(aq) and Na(OH,ClO$_4$)(aq) media at constant ionic strength. Additional measurements were performed in concentrated NaOH(aq) and KOH(aq) solutions at 25 °C without the addition of background electrolyte. The data so obtained have been used to test and refine thermodynamic solubility models of CuO(s) and to quantify the chemical speciation of Cu(II) in alkaline solutions under conditions relevant to the Bayer process.

2. Experimental

All reagents were of analytical grade, purchased from Sigma-Aldrich (USA), Merck (Germany) or Chem Supply (Australia), and used as received. All solutions were prepared using high purity water (Ibis Technology, Perth, Western Australia) that had been deoxygenated and decarbonated by boiling under high purity N_2(g) for 20 minutes. Highly concentrated stock solutions of LiOH(aq), NaOH(aq) and KOH(aq) were prepared so that their carbonate content could be minimised (to $\lesssim$ 0.1 % of total alkalinity) using established methods (Sipos et al., 2000b). Hydroxide and carbonate concentrations were determined (±0.2 %) by titration against standard HCl(aq) (BDH, Convol) and/or Raman spectroscopy (Rudolph and Hefter, 2009). Concentrated stock solutions of $LiClO_4$(aq) and $NaClO_4$(aq) were prepared by weight and analysed by evaporative gravimetry. The sample of CuO(s) used for the solubility studies was obtained from Aldrich (<5 μm, 99+%, ACS).

The solubility of CuO(s) was measured in various hydroxide solutions, as outlined below, using the apparatus described in detail elsewhere (Capewell et al., 1999). Briefly, known masses (ca. 500 to 750 mg) of CuO(s) and appropriate volumes of the alkaline solution, typically ~35 mL, were placed in 50 mL Luer-lock polypropylene syringes which were capped at the tip, closed with a tight-fitting polypropylene piston fitted with a PTFE O-ring, and attached to a carousel immersed in the thermostat bath at the desired temperature (25.00 °C or 59.96 °C). The bath temperature was held constant to ±0.01 °C with an accuracy of ±0.02 °C, monitored using a NIST-traceable quartz crystal thermometer (Hewlett-Packard 2804 A). The syringes were then rotated at ~0.1 rpm so that the solid particles gently percolated through the solution with minimal abrasion. Measurements were performed in duplicate and solutions were sampled over appropriate time intervals until equilibrium was attained.

Prior to sampling, the syringes were kept upright in the bath for ca. 5 min at the equilibration temperature. Solutions were then filtered (0.45 µm GHP Acrodisc, PALL Corporation, USA) into a receiving syringe, also immersed in the bath to maintain their temperature, by the application of hydraulic pressure to the piston in the sample syringe (Capewell et al., 1999). UV-Vis spectra of the samples so obtained were recorded with a HP 8453 diode-array spectrophotometer. Total dissolved copper concentrations in the equilibrated solutions, $[Cu]_T$, were determined to ±4 % using a GBC 933 Flame Atomic Absorption Spectrometer (FAAS) with an air/acetylene flame and an ICP001-Varian Vista AX Inductively Coupled Plasma – Atomic Emission Spectrometer (ICP-AES). The filtered samples were diluted with ultrapure water and then acidified with concentrated nitric acid. Copper standards (1 to 15 ppm) were prepared by dilution of a (1001 ± 2) ppm Cu standard solution (Merck) with 0.5 % w/w HNO_3.

The sample of CuO(s) used for the solubility studies was characterised with a GBC Emma X-ray powder diffractometer (XRD), using CuKα radiation and 2θ scans from 10 to 90 ^{o}, and was found to consist solely of tenorite (ICDD PDF 00-001-1117). Diffraction patterns were also recorded for the equilibrated solid at the end of each solubility experiment. Scanning electron microscope (SEM) images and energy dispersive X-ray (EDX) analyses of the CuO(s) were also obtained before and after equilibration using a JEOL JED-2330 energy dispersive X-ray spectrometer. The BET surface area of the CuO(s) was determined to be 1.38 $m^2 g^{-1}$ with a Micromeritics TriStar II 3020 surface area analyser.

3. Results and Discussion

The results of the present study are summarized in Tables 1 – 4. Solubility measurements were mostly made at constant I in perchlorate media (Tables 1 – 3) to minimise activity coefficient variations. However, a number of measurements were also made in highly concentrated (≥ 6 mol kg^{-1}) MOH(aq) alone (M^+ = Na^+ and K^+; Table 4) so as to provide direct comparisons with the older data (Müller, 1923; McDowell and Johnston, 1936) and with each other at high concentrations (for reasons that will become apparent) and because $KClO_4$ is only sparingly soluble in water.

3.1. Cation effects on the solubility of CuO(s) in alkaline solutions

The solubility of CuO(s) was measured in 5 mol kg^{-1} LiOH(aq) (Table 3) and varying concentrations of NaOH(aq) and KOH(aq) (Table 4) at 25 °C as a function of time. At 25 °C dissolution equilibrium was essentially attained within 24 h and even more quickly at 60 °C; however, the suspensions were always allowed to equilibrate for at least 6 days in all of the solutions evaluated.

The equilibrium solubility of CuO(s), measured as $[Cu^{2+}]_T$, was found to decrease in the order LiOH(aq) >> NaOH(aq) > KOH(aq) at a given temperature and approximately constant $[OH^-]_T$. As would be expected, these results (Tables 1 – 4) were consistent with the UV-Vis spectra of the saturated solutions (Figure 1), which show absorbance maxima in the same order. The spectra are virtually identical in all three media with $\lambda_{max} \approx 638$ nm and $\varepsilon_{max} = 36$ mol^{-1} L cm^{-1} (3.6 m^2 mol^{-1}) corresponding to the single *d-d* transition expected for Cu(II) and consistent with the spectrum previously reported for $Cu(OH)_4^{2-}$(aq) (Norkus et al., 2003).

X-ray diffraction measurements of the CuO(s) before and after equilibration with MOH(aq) indicated the crystal phase to be unaltered tenorite throughout. Before-and-after SEM images and EDX analyses of the CuO(s) also did not reveal any significant differences. It follows that the observed variations of *S* in MOH(aq) reflect differences in the hydration of the cations, in ion pairing between M^+(aq) and $Cu(OH)_4^{2-}$(aq), in activity coefficient effects, and possibly the complexing of M^+(aq) by OH^-(aq) (Baes and Mesmer, 1976). It is interesting to note that the solubility of goethite (FeOOH(s)) is also much higher in LiOH(aq) than in other caustic solutions at the same $[OH^-]_T$ and temperature, and with the same solubility sequence (LiOH(aq) > NaOH(aq) > KOH(aq)) at 25 °C (Kamnev et al., 1986) as established here for CuO(s).

The solubility of CuO(s) in LiOH(aq) solution does not appear to have been reported previously but there have been a number of studies in NaOH(aq) and KOH(aq) (Müller, 1923; McDowell and Johnston, 1936; Akhmetov et al., 1967; Baes and Mesmer, 1976). A comparison of these solubilities indicates that some of them are significantly higher than the present values at 25 °C. The reasons for this are discussed below (Section 3.4).

3.2. Solubility of CuO(s) in MOH(aq) at constant I: formation of $Cu(OH)_4^{2-}(aq)$

Solubility measurements are a reliable, if not very precise, method for quantifying complex equilibria, often working when all other methods fail (Königsberger and Gamsjäger, 2003; Hefter, 2013). The increase in solubility of CuO(s) with increasing $[OH^-]_T$ (Tables 1 – 4) is undoubtedly due to the formation of relatively-soluble higher-order complexes. Ignoring the possible formation of 'polynuclear' species, which is reasonable given the low $[Cu(II)]_T$ and high $[OH^-]_T/[Cu(II)]_T$ ratios, the dissolution of CuO(s) in strongly alkaline solutions can be written

$$CuO(s) + nOH^-(aq) + H_2O(aq) \rightleftharpoons Cu(OH)_{(2+n)}^{n-}(aq)$$

for which the equilibrium constant is (assuming activity coefficients are constant at constant I)

$$K_{s(n+2)} = \frac{[Cu(OH)_{(n+2)}^{n-}]}{[OH^-]^n}$$

Assuming all dissolved copper is present as $Cu(OH)_4^{2-}$ (aq), the observed solubility is

$$S = [Cu]_T = [Cu(OH)_4^{2-}]$$

and given that $[Cu(OH)_4^{2-}] << [OH^-]$, it follows that $[OH^-] \approx [OH^-]_T$, so that

$$\log S = \log K_{s4} + 2 \log [OH^-]_T$$

Therefore a plot of $\log S$ against $\log [OH^-]_T$ should be linear with a slope of exactly 2 and an intercept of $\log K_{s4}$.

For solubility measurements to be useful for quantifying equilibria it is essential to keep activity coefficients as constant as possible while varying the concentrations of the interacting species. This is done by making the usual (albeit imperfect) assumption that activity coefficients depend only on I, the total (stoichiometric) ionic strength of the solution. Accordingly, the solubility of CuO(s) was determined at (25.00 and 59.96) ^{o}C as a function of $[OH^{-}]_T$ at $I = 5.00$ mol kg^{-1} in $Na(ClO_4)$ and $Li(ClO_4)$. Measurements were also made at $I = 6.00$ mol kg^{-1} $Na(ClO_4)$ at 25 ^{o}C for comparison purposes. The results obtained are summarized in Tables 1 – 3.

A typical plot of log $[Cu]_T$ vs. log $[OH^{-}]_T$ is shown in Figure 2. The line of best fit shows good linearity ($R^2 = 0.997$), although the slope is slightly higher than 2.00 and there is a slight hint of upward curvature with increasing $[OH^{-}]_T$. This may indicate the formation of small amounts of $Cu(OH)_5^{3-}$(aq) or, equally likely, a partial breakdown of the various assumptions made. The increase in solubility of CuO(s) in MOH(aq) at $I = 5$ mol kg^{-1} $M(ClO_4)$, where $M^{+} = Li^{+}$ and Na^{+}, with temperature is reflected by an increase in log K_{s4}. The values obtained for n and log K_{s4} under the various conditions are summarized in Table 5.

3.3. Solubility modelling

Plyasunova et al. (1997) evaluated Cu(II) hydrolysis equilibria and reported (i) standard enthalpies of formation and standard entropies for CuO(s), Cu^{2+}(aq) and various Cu(II)-hydroxo complexes and (ii) a set of SIT interaction parameters (Grenthe et al., 1997). The average value of log $K_{s4}°$ = –4.10 ± 0.16 at 25 °C, evaluated by Plyasunova et al. (1997), was essentially based on McDowell and Johnston's (1936) solubility data in KOH(aq) and NaOH(aq). In a recent critical review for IUPAC, Powell et al. (2007) noted deficiencies in the SIT analysis (Plyasunova et al., 1997) but nevertheless used the log $K_{s4}°$ value of Plyasunova et al. (1997) for the evaluation of their recommended log $\beta_4°$ value, which was found to be in only fair agreement with other data (Powell et al., 2007, p. 905).

Accordingly, the model selected by Plyasunova et al. (1997) was used as a starting point for the thermodynamic analysis of the present CuO(s) solubilities in MOH(aq) solutions. Preliminary solubility calculations using the ChemSage software (Eriksson and Hack, 1990) indicated that, in agreement with the data in Figure 2, only $\mathrm{Cu(OH)_4^{2-}}$(aq) was significant under the experimental conditions employed in this work. The ChemSage optimiser (Königsberger and Eriksson, 1995) was then used to process the experimental solubility data obtained in this study at 25 °C, adjusting simultaneously the enthalpy of formation for $\mathrm{Cu(OH)_4^{2-}}$(aq) and the SIT parameters $\varepsilon(\mathrm{M^+}, \mathrm{Cu(OH)_4^{2-}})$, where $\mathrm{M^+} = \mathrm{Li^+}$, $\mathrm{Na^+}$, $\mathrm{K^+}$. For this optimisation, the SIT parameters for the alkali metal hydroxides and perchlorates were taken from Table IX.2 of Grenthe et al. (1997) (noting that slightly different parameters were employed by Plyasunova et al. (1997)). The resulting SIT parameters, $\varepsilon(\mathrm{M^+}, \mathrm{Cu(OH)_4^{2-}})$, were –0.185 ($\mathrm{Li^+}$) , 0.044 ($\mathrm{Na^+}$) and 0.073 ($\mathrm{K^+}$), and correspond to a decrease in the $\mathrm{M^+{-}Cu(OH)_4^{2-}}$ interaction in the order $\mathrm{Li^+{-}Cu(OH)_4^{2-}} > \mathrm{Na^+{-}Cu(OH)_4^{2-}} > \mathrm{K^+{-}Cu(OH)_4^{2-}}$. The standard solubility constant, $K_{s4}°$, for $\mathrm{Cu(OH)_4^{2-}}$ at 25 °C, resulting from the present optimisation, log $K_{s4}°$ = –4.88, is significantly lower (more negative) than the value, log $K_{s4}°$ = –4.10, obtained by Plyasunova et al. (1997) from McDowell and Johnston’s (1936) solubility data.

3.4. Comparisons with earlier studies

The solubilities of CuO(s) at ~18 °C in very high concentrations (converted to molalities using the density data of Sipos et al., 2000a) of NaOH reported by Müller (1923) agree very well with the present values at 25 °C (Figures 3 and 4). However, those of McDowell and Johnston (1936) measured in KOH(aq) at 25 °C (five solubility data points were also reported in NaOH(aq)) are mostly significantly higher than those obtained under comparable conditions in this work. Indeed, they almost approach the present CuO(s) solubilities in Li(OH,ClO_4)(aq) (Figure 3). Such large discrepancies are unlikely to be due solely to experimental errors.

The differences between the present solubilities of CuO(s) and those of McDowell and Johnston (1936) appear to be best explained by particle size effects. It has long been known, but frequently forgotten, that the measured solubility of solids increases with decreasing particle size below a certain value (corresponding to the macroscopic solubility limit). Schindler et al. (1965) have made a detailed study of the solubility of CuO(s) in aqueous solution as a function of particle size (expressed in terms of molar surface area). Samples of CuO(s) prepared by precipitation from boiling water/methanol solution (Schindler et al., 1965) had the smallest particle size (BET surface area 4340 m^2 mol^{-1}) and the highest measured solubility. Other samples were prepared by annealing the dried solid for 6 hours at progressively increasing temperatures up to 600 °C. The sample obtained at the highest temperature exhibited the largest particle size (BET surface area 230 m^2 mol^{-1}) and the lowest solubility (by a factor of ca. 2.2 cf. the freshly precipitated sample), which was taken to be the true (macroscopic or ‘bulk’) thermodynamic value (Schindler et al., 1965).

The CuO(s) sample used in the present study had a very low surface area (110 m^2 mol^{-1}) and is thus expected to have a solubility that corresponds to the macroscopic (thermodynamic) value. For their solubility measurements, McDowell and Johnston (1936) used a CuO(s) sample that was freshly precipitated from boiling aqueous solution, which would therefore be expected to have a small particle size. Indeed, their results in NaOH(aq) exceed the present values by about a factor of 2 at low NaOH concentrations (Figure 3), where the solubility of CuO(s) is low and therefore may be strongly influenced by the extent of dissolution of small particles. However, at high NaOH concentrations where the solubility is higher, the more soluble small particles are more likely to have dissolved, causing the measured solubility to be controlled by the larger ‘bulk’ particles. Under these conditions McDowell and Johnston’s results approach the present values (Figure 3). This finding, and the agreement with the data of Müller (1923), is broadly consistent with Schindler et al. (1965) who suggested that the effect of particle size should be less pronounced in alkaline solutions.

Particle-size effects thus account straightforwardly for the higher measured solubilities of McDowell and Johnston (1936). It follows that the analysis of Plyasunova et al. (1997) based on such data must yield a result for the standard solubility constant, $K_{s4}°$, that is too high.

It is noteworthy that a single value for the SIT parameter, $\varepsilon(\mathrm{Li}^+, \mathrm{Cu(OH)}_4^{2-}) = -0.185$, was sufficient to correlate CuO(s) solubilities in LiOH(aq) at 25 °C and 60 °C, whereas calculations using the $\varepsilon(\mathrm{Na}^+, \mathrm{Cu(OH)}_4^{2-})$ value determined at 25 °C overestimated CuO(s) solubilities measured at higher temperatures. This is a reminder that SIT is at best a useful approximation of speciation behaviour with a limited ability to predict outside of its parameterization space.

4. Conclusions

Solubility measurements of well-characterised CuO(s), tenorite, in alkaline media, supported by UV-Vis spectra, established that (i) the solubility equilibrium is attained quickly (usually within 1 day); and also that the solubility of CuO(s): (ii) varies in the order LiOH >> NaOH > KOH, (iii) increases with $[\mathrm{OH}^-]_\mathrm{T}$ in solutions at, or not at, constant I; and (iv) increases with the temperature at least up to 60 °C. It was also shown that some of the older solubility data in the literature (McDowell and Johnston, 1936) are probably too high because of particle-size effects. The predominant Cu(II) species in concentrated MOH(aq) solutions, was found to be $\mathrm{Cu(OH)}_4^{2-}$(aq) under all conditions studied. No changes of the solid phase were detected by XRD, SEM or EDX analyses at the conclusion of the solubility experiments. Using a SIT model, CuO(s) solubilities could be correlated with good precision up to high alkali hydroxide concentrations. In Li(OH,$\mathrm{ClO_4}$)(aq), but not in Na(OH,$\mathrm{ClO_4}$)(aq), a single temperature-independent SIT parameter suffices to model solubilities at both (25 and 60) °C.

The present results suggest that, for typical caustic concentrations, CuO(s) solubilities in Bayer liquors at precipitation temperatures, usually ~ (50 to 70) °C, are in the order of (0.1 to 2) mmol L^{-1}. Such concentrations are of industrial significance given the possible role of dissolved copper in various redox reactions. In addition, the likely interaction of soluble copper species with sulfide has obvious consequences for the control of various impurities in Bayer liquors (e.g., mercury) on account of their environmental and industrial health implications.

Acknowledgements

This work was funded by Alcoa World Alumina, BHP Billiton/Worsley Alumina, Hydro Aluminium, Rio Tinto Alcan/QAL and AMIRA International via its collaborative research project P507D, 'Chemistry and Transport of Trace Element in Bayer Liquors'. We thank Dr. Marc Hampton for performing the SEM and EDX analyses and Dr. Danielle Meyrick for helpful suggestions. Critical comments by two anonymous reviewers are gratefully acknowledged.

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Table 1: Solubility of CuO(s) in {NaOH(aq) + $NaClO_4$(aq)} mixtures of ionic strength I = 6.00 mol kg^{-1} at 25.00 °C. The estimated uncertainty in $[Cu^{2+}]_T$ is ± 4 %.

[NaOH]/mol kg^{-1}	10^5 $[Cu^{2+}]_T$ /mol kg^{-1}
0.50	1.40
0.75	3.23
1.00	6.03
1.50	11.5
2.00	20.7
2.50	36.9
3.00	55.4
4.00	118
5.00	179
6.00	251

Table 2: Solubility of CuO(s) in {NaOH(aq) + $NaClO_4$(aq)} mixtures of ionic strength I = 5.00 mol kg^{-1} at 25.00 °C and 59.96 °C. The estimated uncertainty in $[Cu^{2+}]_T$ is ± 4 %.

[NaOH]/mol kg^{-1}	$10^5\ [Cu^{2+}]_T$ /mol kg^{-1}	
	25 °C	60 °C
0.50	2.15	3.23
1.00	5.51	6.07
2.00	22.7	30.5
3.00	54.1	63.3
4.00	101	116
4.99	168	186

Table 3: Solubility of CuO(s) in {LiOH(aq) + $LiClO_4$(aq)} mixtures of ionic strength I = 5.00 mol kg^{-1} at 25.00 °C and 59.96 °C. The estimated uncertainty in $[Cu^{2+}]_T$ is ± 4 %.

[LiOH]/mol kg^{-1}	10^5 $[Cu^{2+}]_T$ /mol kg^{-1}	
	25 °C	60 °C
0.50	5.13	7.10
1.00	17.4	24.0
2.00	71.6	100
3.00	170	235
4.00	308	428
5.00	538	707

Table 4: Solubility of CuO(s) in high concentrations of NaOH(aq) and KOH(aq) at 25.00 °C. The estimated uncertainty in $[\mathrm{Cu}^{2+}]_\mathrm{T}$ is ± 4 %.

$[\mathrm{NaOH}]/\mathrm{mol\ kg}^{-1}$	$[\mathrm{KOH}]/\mathrm{mol\ kg}^{-1}$	$10^5\ [\mathrm{Cu}^{2+}]_\mathrm{T}\ /\mathrm{mol\ kg}^{-1}$
8.00	–	424
10.00	–	660
12.00	–	971
14.00	–	1509
16.00	–	1970
–	6.00	184
–	8.00	250
–	10.00	320

Table 5. Solubility constant, log K_{s4}, and slope n for CuO(s) in {NaOH(aq) + $NaClO_4$(aq)} and {LiOH(aq) + $LiClO_4$(aq)} mixtures of constant ionic strength I at (25.00 and 59.96) °C, as derived from linear regression of log ($[Cu^{2+}]_T$/mol kg^{-1}) *vs.* log ($[OH^-]_T$/mol kg^{-1}).

I	θ/ °C	n	log K_{s4}	R^2
5.00 mol kg^{-1} ($LiClO_4$)	25.00	2.08	−3.71	0.994
	59.96	2.03	−3.58	1.000
5.00 mol kg^{-1} ($NaClO_4$)	25.00	2.12	−4.27	0.999
	59.96	2.11	−4.19	0.998
6.00 mol kg^{-1} ($NaClO_4$)	25.00	2.11	− 4.25	0.997

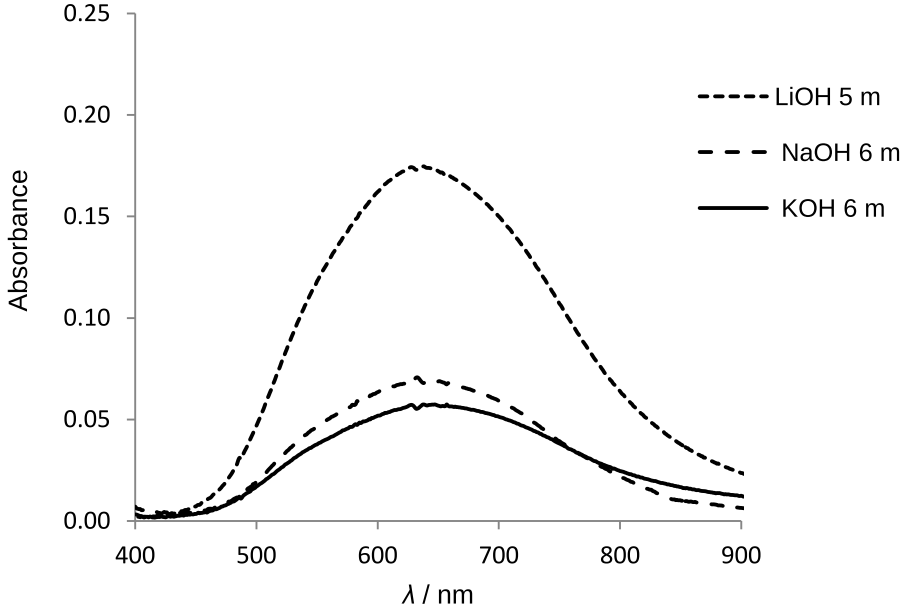

Figure 1. Comparisons of UV-Vis spectra of saturated CuO(s) solutions in Li^+, Na^+ and K^+ hydroxide solutions at 25 ^oC.

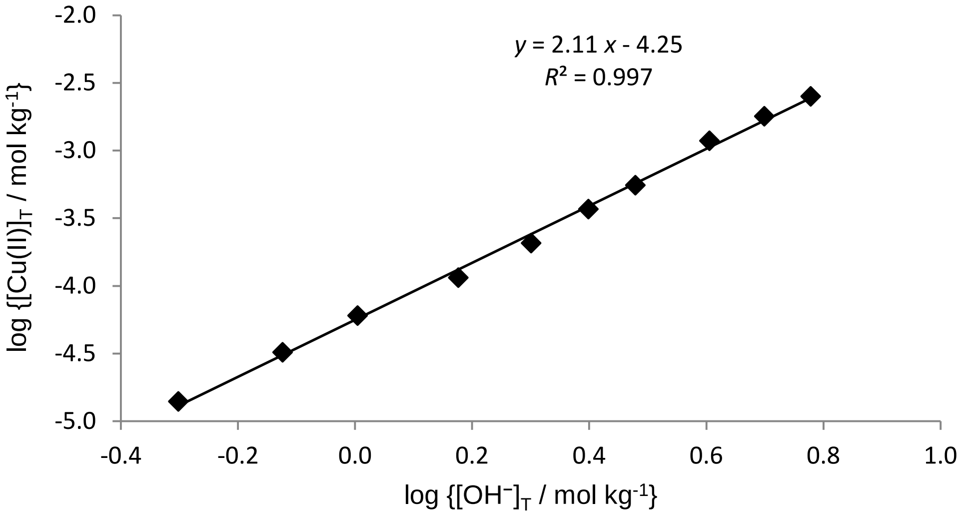

Fig. 2. Plot of log $[Cu(II)]_T$ versus log $[OH^-]_T$ for the solubility of CuO(s) in 6 mol kg^{-1} {NaOH(aq) + $NaClO_4$(aq)} mixtures at 25 °C.

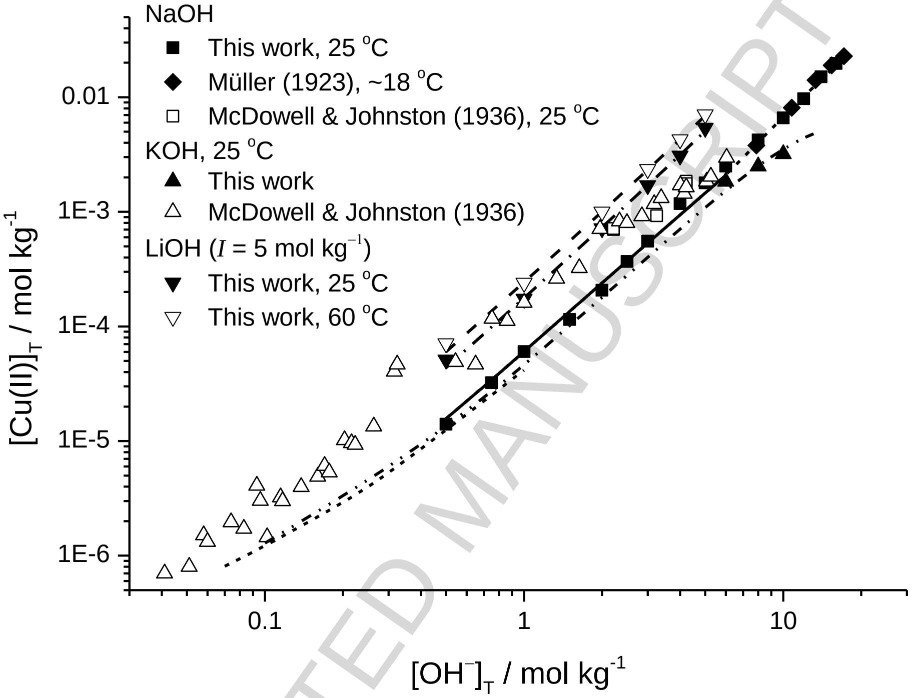

Figure 3: Solubility of CuO(s) in alkali metal hydroxide solutions measured in this work and reported in the literature (Müller, 1923; McDowell and Johnston, 1936). The lines were calculated using the present SIT model: solid, $I = 6$ mol kg^{-1} {NaOH(aq) + $NaClO_4$(aq)} at 25 °C; dotted, NaOH(aq) at 25 °C; dash-dot-dot, KOH(aq) at 25 °C; dash-dot, $I = 5$ mol kg^{-1} {LiOH(aq) + $LiClO_4$(aq)} at 25 °C; dashed, $I = 5$ mol kg^{-1} {LiOH(aq) + $LiClO_4$(aq)} at 60 °C.

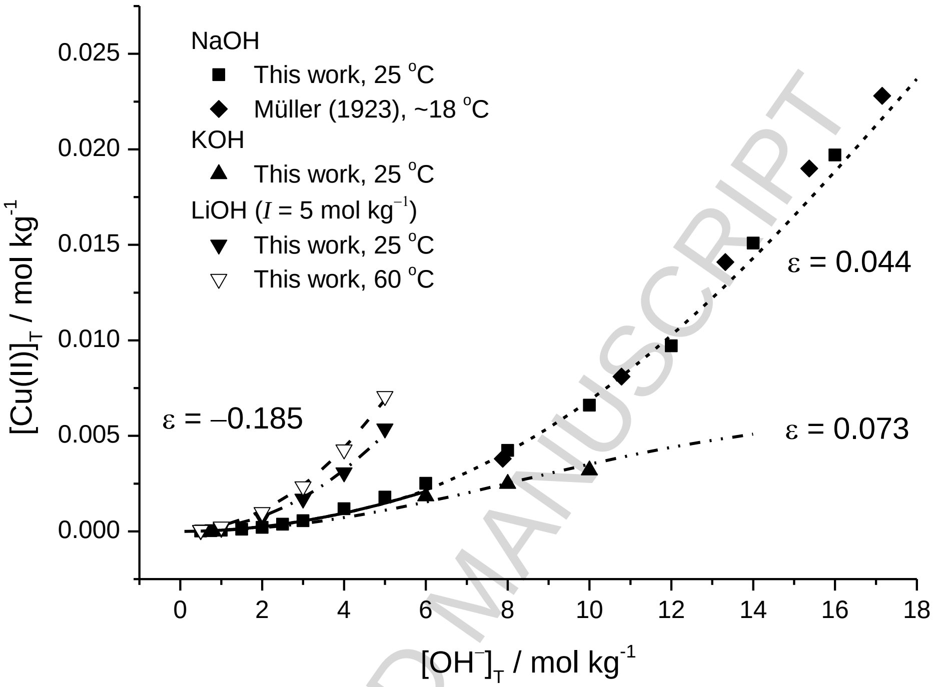

Figure 4: Solubility of CuO(s) in alkali metal hydroxide solutions measured in this work and reported in the literature (Müller, 1923). The lines were calculated using the present SIT model: solid, I = 6 mol kg^{-1} {NaOH(aq) + NaClO$_4$(aq)} at 25 °C; dotted, NaOH(aq) at 25 °C; dash-dot-dot, KOH(aq) at 25 °C; dash-dot, I = 5 mol kg^{-1} {LiOH(aq) + LiClO$_4$(aq)} at 25 °C; dashed, I = 5 mol kg^{-1} {LiOH(aq) + LiClO$_4$(aq)} at 60 °C.

Highlights

- CuO (tenorite) solubilities (*S*) were measured in alkaline media at 25 and 60 °C.
- *S* increased (i) in the order KOH < NaOH << LiOH and (ii) with temperature.
- At constant ionic strength, linear plots of log *S* vs. log $[OH^-]$ had a slope of 2.0.
- Consequently, consistent with UV-Vis spectra, only $Cu(OH)_4^{2-}$ (aq) was significant.
- Using a SIT model, *S* could be described well up to high $[OH^-]$ in all media.