Carbonate removal from concentrated hydroxide solutions

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Methods for routinely lowering the carbonate content of concentrated aqueous hydroxide solutions [MOH with M^+ = Li^+, Na^+, K^+, Cs^+ and $(CH_3)_4N^+$] to analytically negligible levels ($\leq$ 0.2% of the total alkalinity) are described. No single method was satisfactory for all MOH. Carbonate can be removed from highly concentrated (*ca.* 50% w/w) NaOH solutions by filtration since Na_2CO_3 is almost insoluble in this medium. However, for LiOH (*ca.* 4 M), $(CH_3)_4NOH$ (*ca.* 4.5 M) and KOH (*ca.* 14 M) and less concentrated NaOH ($<$10 M), treatment with excess solid CaO followed by filtration gave the best results. For CsOH, which may be seriously contaminated with carbonate, the only satisfactory procedure was treatment of very concentrated solutions with excess solid $Ba(OH)_2$. Residual calcium and barium concentrations in the decarbonated solutions were at trace levels.

Introduction

The determination of acids by titration against standard aqueous hydroxide solutions is a cornerstone of analytical chemistry. Standard hydroxide solutions are also widely used for the study of complex equilibria and in chemical synthesis. Typically, NaOH and KOH are employed for such purposes although the other alkali metal and the tetraalkylammonium hydroxides [such as $(CH_3)_4NOH$ (TMAOH)] also find application.

The most common impurity (besides water) in commercial solid hydroxides is carbonate due to adsorption of atmospheric $CO_2(g)$. The carbonate imputity level is usually 2–3% w/w although commercial CsOH samples may contain as much as 15% w/w. As carbonate ($CO_3{}^{2-}$) undergoes protonation in the middle of the aqueous pH range ($\log K_{a_1}$ = 9.57 and $\log K_{a_2}$ = 6.02 at I = 1 M and 298 K[1]), complexes many metal ions[1] and interferes with the operation of some indicators,[2] its removal is imperative for serious titrimetric analyses.

Numerous methods have been described for the preparation of carbonate-free alkali solutions. The most common are listed below.

1. *Prior* to bulk dissolution, solid NaOH or KOH (in pellet or stick form) is quickly rinsed with water,[2,3] which dissolves the surface, thereby removing most of the carbonate. This technique is simple, rapid and reasonably effective. However, it removes only the surface carbonate, is applicable only to those hydroxides available in massive form, is wasteful and, in inexperienced hands, may result in poor quality solutions.

2. Carbonate can be removed from highly concentrated sodium hydroxide solutions by the salting out of Na_2CO_3.[4] Typically,[2,5] a 50% w/w (*ca.* 20 M) aqueous NaOH solution is prepared and allowed to stand for at least 2 d. Part of the $Na_2CO_3(s)$ settles while some forms a solid crust on the solution surface. 'Carbonate-free' NaOH solution is then obtained by decantation or syphoning of the supernatant and diluted to the desired concentration. This method is satisfactory for NaOH but cannot be used for other MOH solutions, because their carbonates are too soluble (KOH and CsOH) or because the solubility of the base is too low to salt out the carbonate (LiOH and TMAOH).

3. High purity aqueous solutions of MOH have been produced[2] by the decomposition of alkali metal amalgams, generated by the electrolysis of an appropriate salt at a mercury pool cathode. This method is satisfactory but slow and it is not suited to the production of highly concentrated solutions.

4. Carbonate may be removed from dilute alkali solutions by anion exchange.[2] This technique, however, cannot be used for concentrated base solutions as they attack the resin.

5. Carbonate has occasionally been removed from NaOH by recrystallization,[6] but most MOH are too soluble for this approach.[7] Furthermore, the procedure is wasteful and the handling of hot concentrated alkaline solutions is problematic.

6. Alkaline earth metal oxides or salts can be added to concentrated base solutions to precipitate the sparingly soluble alkaline earth metal carbonates which can then be removed by filtration.[8] This technique is most suitable if the alkaline earth metal hydroxide is also of low solubility. For example, $Ba(OH)_2$ is known[5] to remove carbonate from dilute ($<$1 M) aqueous KOH, but this treatment must be combined with an ion-exchange step to remove the dissolved Ba^{2+} because of the relatively high solubility of $Ba(OH)_2$. Industrially, CaO(s) is used to remove carbonate from Bayer liquors[9] in a step known as causticization:

$$CaO(s) + H_2O + Na_2CO_3(aq.) \rightarrow CaCO_3(s) + 2\ NaOH(aq.)$$
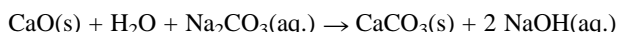
During recent studies[10–13] employing a range of highly concentrated alkali metal solutions we found that many of the common methods for carbonate removal were ineffective. Accordingly, an investigation was undertaken to develop and verify techniques to remove carbonate, to analytically insignificant levels, from concentrated aqueous MOH solutions (M^+ = Li^+, Na^+, K^+, Cs^+ and TMA^+).

Experimental

Materials

Concentrated alkali metal stock standard solutions were prepared from analytical-reagent grade NaOH (98%) (Ajax Chemicals, Seven Hills, NSW, Australia), KOH (85% w/w with *ca.* 10–15% w/w water) (Ajax), LiOH·H_2O (99%+) (Sigma–Aldrich Chemical Co., St. Louis, MO, USA), CsOH·H_2O (99.5%+) (Sigma–Aldrich) and TMAOH·5H_2O (97%+) (Sigma–Aldrich). TMAOH solutions were also obtained as concentrated analytical-reagent grade solutions (25% w/w, Sigma–Aldrich). The approximate concentrations of the stock standard solutions were NaOH $\approx$ 8 or 20 M, KOH $\approx$ 14 M, LiOH $\approx$ 4.8 M, CsOH $\approx$ 12 or 15 M and TMAOH $\approx$ 2.8 or 4.5 M.

Analytical-reagent grade CaO (99.9%, Sigma–Aldrich) and $Ba(OH)_2 \cdot 8H_2O$ (99%+) (Ajax) were used without further purification. All the other chemicals were of analytical-reagent grade. All solutions were prepared with water from a Milli-Q system (Millipore, Bedford, MA, USA). Where relevant, the Millipore water was rendered free of CO_2 by boiling while purging with high purity nitrogen for at least 20 min. After preparation, the base solutions were stored in airtight plastic or Pyrex-glass containers equipped with a soda-lime CO_2 trap. It is worth noting that Pyrex (as opposed to soda glass) shows very little reactivity towards alkaline solutions at ambient temperatures. No visible signs of deterioration were observed for highly concentrated base solutions stored in Pyrex vessels at ambient temperature over long periods.

Measurements

The exact concentrations of the base solutions and their carbonate content were determined by high precision glass electrode potentiometric titrations following the procedures described in detail previously.[14] Concentrated stock standard solutions were appropriately diluted to give a total hydroxide concentration $[OH^-]_T \approx 0.1$ M *via* accurate weighing (without buoyancy correction). The samples were made up to an ionic strength $I = 1$ M (NaCl), where $I = 0.5\Sigma c_i z_i$.[2] Aliquots (10–25 mL) of these solutions were then titrated with standard acid solutions of the same ionic strength, prepared from commercial volumetric ampoules [Convol (BDH, Poole, Dorset, UK), stated accuracy ±0.2%]. The titrations were evaluated by the Gran method[15] and the ESTA suite of computer programs.[16]

Solution densities were measured (to ±5 μg cm^{-3}) by using an Anton-Paar (Graz, Austria) DMA 02D precision density meter at 25.0 ± 0.02 °C. Air and distilled water were used as density standards. Where required, trace element concentrations in the decarbonated alkaline stock standard solutions were measured by ICP-AES. Raman spectra of some stock standard solutions, sealed in small glass vials, were obtained with a Bruker (Karlsruhe, Germany) RFS-100 Fourier transform Raman spectrometer with an Nd:YAG (1064 nm) laser and a Ge-diode detector using 200 mW laser power, 512 scans and 4 cm^{-1} resolution.

Results and discussion

Very concentrated (> 10 M) NaOH solutions

As noted above, it is well known that Na_2CO_3 is virtually quantitatively salted out of highly concentrated NaOH solutions (> 10 M or 25% w/w) even at ambient temperatures.[7] However, decantation or syphoning of the supernatant (after preparation and settling), recommended many years ago by Sillen's group,[5] was found to be unreliable in our hands. More consistent results were obtained by vacuum filtration. For this, a 0.45 μm pore-size caustic-resistant supported membrane filter (Versapor 450) was placed in a polysulfone (Nalgene) filter unit. During filtration the solution was separated from the atmosphere with a CO_2 trap containing soda-lime. The filtrate was collected in a Pyrex vessel. This method routinely produced concentrated NaOH solutions with carbonate concentrations < 0.2% of the total alkalinity. The advantage of this technique is that short exposure of the resultant solution to atmospheric CO_2 does not introduce any serious error in the concentration of the stock standard solutions prepared this way. The disadvantages are that the concentrated NaOH solutions are difficult to manipulate because of their high viscosity and that the crystallization of the $Na_2CO_3(s)$ is usually slow. This means it is vital to allow

sufficient time (days or possibly weeks) for precipitation to be completed.

Moderately concentrated (< 10 M) NaOH solutions

Moderately concentrated NaOH solutions, in which Na_2CO_3 is appreciably soluble,[4] are better rendered carbonate-free by precipitation of $CaCO_3(s)$ following treatment with excess of CaO(s). This procedure relies upon the sparing solubility of both $Ca(OH)_2(s)$ and $CaCO_3(s)$ in concentrated NaOH solutions.[11,17,18] The NaOH solution (*ca.* 8 M) is prepared in the usual way and CaO(s) is added (2 g per litre of solution) and the mixture stirred vigorously overnight in an appropriate airtight container. The solution is kept for 2–4 d to allow the solids to settle. The solution is then passed through a supported membrane filter (as above). A typical standardisation of such a solution is shown in Fig. 1, which demonstrates that the resultant solutions have carbonate concentrations below the potentiometric detection limit (*ca.* 0.05% of the total alkalinity). Analysis by ICP-AES indicated that the average residual calcium concentration in the filtered solutions was insignificant (< 1 ppm, or $< 2.5 \times 10^{-5}$ M).

Use of CaO(s) for more concentrated (> 10 M) NaOH solutions is not recommended. The solids produced are very fine and filtration of the highly viscous slurries is problematic; the membrane filter often becomes blocked and filtration can take several days. Such lengthy exposure of the filter to concentrated caustic solutions is inadvisable.

Other aqueous MOH solutions (M$^+$ = K$^+$, Li$^+$ and TMA$^+$)

Treatment of other MOH solutions (M$^+$ = K$^+$, Li$^+$ and TMA$^+$) with CaO(s) was also investigated. As described previously,[17] treatment of *ca.* 0.1 M TMAOH solutions (in the presence of 1–5 M TMACl) with CaO(s) resulted in solutions with carbonate concentrations of < 0.2% of the total alkalinity. Similar levels of carbonate can be obtained by CaO(s) treatment of more concentrated (≤4.5 M) TMAOH. The residual calcium concentration of the solutions varied according to the nature of the MOH solution and its concentration (increasing with decreasing [MOH]) but was always ≤1 ppm. It is appropriate to mention that TMA$^+$ compounds are prone to contain proton-
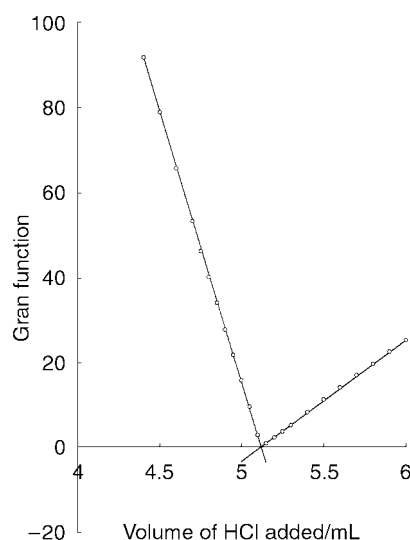
Fig. 1 Gran plot of a pH-potentiometric titration. Vessel, 10.00 mL of 0.1024 M NaOH in $I = 1$ M Na(Cl); burette, 0.2000 M HCl in $I = 1$ M (Na)Cl. The base solution was prepared by dilution of a *ca.* 8 M NaOH solution treated with CaO(s), as described in the text. Note that the least-squares lines of best fit ($r^2 > 0.9997$) are for all data points in the titration, not just those shown.

active (probably amine) impurities[17] which are indistinguishable from carbonate in pH-metric titrations and which cannot be removed by CaO(s) treatment. Such impurities are best removed by recrystallization.[17]

Treatment of concentrated KOH (*ca.* 14 M) and LiOH (*ca.* 4.8 M) solutions with CaO(s), analogous to that described for NaOH, produced solutions with carbonate concentrations < 0.1% of the total alkalinity. The residual calcium concentrations in these concentrated solutions were 1 ppm (KOH) and 12–16 ppm (LiOH), which would be negligible for most applications, particularly after dilution.

CsOH solutions

Glass-electrode titrimetric analysis of CsOH ($[Cs^+]_T \approx 15$ M) solutions prepared from various commercial analytical-reagent grade samples of $CsOH \cdot H_2O(s)$ revealed a carbonate (or carbonate-like) impurity content of up to 15 mol%. This corresponds to a carbonate concentration of up to 1 M! Treatment with excess CaO(s) was ineffective. As such high levels of contamination were unexpected, the Raman spectrum of the solution was recorded. Comparison with that of a 1 M Na_2CO_3 solution (pH 13, Fig. 2) showed the same well-defined peak at around 1060 cm^{-1}, with approximately the same intensity, corresponding to the symmetrical stretching vibration of the carbonate ion.[19] This confirms that the contamination is indeed (at least mostly) carbonate.

A variety of methods for the removal of carbonate from concentrated CsOH solutions were tried and found to be unsuccessful. These included treatment with various solid M(III) and M(II) oxides and hydroxides, recrystallization of $CsOH \cdot H_2O$ and thermal decomposition. In the last case, conversion of Cs_2CO_3 at > 610 °C[20] looked promising but Cs_2O melted at 360–400 °C[20] and reacted with the platinum crucible!

Eventually, the following procedure was adopted: a concentrated 'CsOH' solution ($[Cs^+]_T \approx 12$ M, $[CO_3^{2-}]_T \approx 0.8$ M) was mixed with an excess of $Ba(OH)_2(s)$. The slurry was agitated overnight and allowed to settle (for 2–3 d) and then filtered as described above for NaOH. Subsequent pH-metric analysis indicated a carbonate content < 0.05% of the total alkalinity. As the solubility of $Ba(OH)_2$ in water is fairly high (*ca.* 2 M at 298 K),[20] the filtrate was found to have a residual barium concentration of about 10^{-3} M (*ca.* 140 ppm). This can be lowered by increasing the concentration of the CsOH solution. *e.g.*, a 15 M CsOH solution after treatment had a residual barium concentration of ~ 2 × 10^{-4} M (30 ppm). Given that direct use of such a concentrated solution would be extremely rare, this level of contamination can be considered negligible for most purposes.
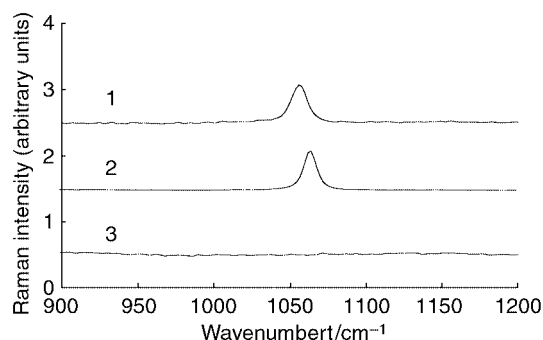
A note on the preparation of dilute MOH solutions

Although it has been found to be most efficient and effective to remove carbonate from concentrated MOH solutions, most analytical procedures utilize much more dilute solutions ($\leqslant 1$ M). For many applications it is very convenient to use commercially available 'concentrated volumetric standards'. Solutions prepared from these commercial ampoules, typically 0.1–1 M in base, have been found routinely to contain $\leqslant 0.1$ mol% carbonate, provided that the usual precautions (the use of CO_2-free water, protection against atmospheric contact, *etc.*) are taken. Alternatively, such solutions are readily prepared by dilution of the more concentrated solutions referred to above. It should be noted, however, that because of the high viscosity of concentrated hydroxide solutions, dilution using conventional pipetting procedures is inaccurate. This difficulty can be circumvented by the use of a piston burette, but this limits the accuracy of dilution to *ca.* 0.1% and is not always convenient. Dilution by direct weighing into a calibrated flask, coupled with determination of the density of the concentrate, has been found to be very convenient. The accuracy and ease of use of modern vibrating tube density meters make this procedure very attractive, although for the highest accuracy (*i.e.*, better than 0.1%), buoyancy corrections must be applied.

Conclusions

No single method removes carbonate from all concentrated hydroxide solutions. The optimum procedure depends on the cation (*i.e.*, on the chemical characteristics of the solution and on the relevant sparingly soluble compounds it forms) and, for NaOH, on the concentration. Nevertheless, procedures that produce concentrated hydroxide solutions with analytically negligible concentrations of carbonate and which result in minimum contamination by other species have been developed for MOH with M$^+$ = Li$^+$, Na$^+$, K$^+$, Cs$^+$ and TMA$^+$. More dilute carbonate-free hydroxide solutions can be prepared by dilution of such solutions.

Acknowledgements

Fig. 2 Raman spectra of (1) an untreated CsOH solution ($[Cs^+]_T \approx 15$ M, $[CO_3^{2-}]_T \approx 1$ M), (2) a 1 M Na_2CO_3 solution at pH 13 and (3) solution from (1) treated with $Ba(OH)_2(s)$. Spectra were background corrected using water as baseline and offset for clarity.

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