Novel synthesis of alkali and quaternary onium hydroxides *via* liquid anion exchange; an alternative concept for the manufacture of KOH and other hydroxide salts

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Alcohols enhance the extraction of a basic potential through a liquid membrane in the presence of quaternary ammonium salts, thus enabling preparation of caustic solutions without direct transport of hydroxide ions.

Production of potassium hydroxide (KOH) in the US in 1993 was 276 kilotons.[1] It is used principally in the manufacturing of K_2CO_3 and $KMnO_4$, and for the production of pesticides, fertilizers, soaps and detergents.[1] Quaternary onium hydroxides are mainly used as phase-transfer catalysts and as templating agents in the synthesis of molecular sieves.[2]

Currently, KOH is produced industrially by the electrolysis of KCl, using diaphragm cells, mercury cells, or ion-exchange membrane cells. Because of high energy costs and product impurities associated with diaphragm cells, most of the KOH is produced using ion-exchange membrane cells or mercury cells. Obviously, environmental awareness is a prime concern in KOH plants employing the latter protocol. Other electrolytic and electrodialytic methods are known for the preparation of MOH-type salts[3,4] and quaternary onium hydroxides[5] on a small and medium scale, but all of these alternatives are capital and energy intensive, with product cost very sensitive to plant size.

We have previously shown that quaternary ammonium hydroxides could also be produced on a laboratory scale in a batch solid-liquid extraction process.[6] However, since it was necessary to use a methanolic solution, no phase separation was obtained, leading to a complicated protocol which precluded large-scale applications.‡

It is well known that direct liquid/liquid extraction of hydroxide anions using onium salts is practically impossible.[7] However, we have now discovered[8] that contacting a weak organic acid ($pK_a > 16$; *e.g.* an alcohol) with a quaternary onium halide in a hydrophobic medium, creates a liquid membrane that can selectively extract and release a basic potential between two aqueous solutions. This enables the preparation of various hydroxide salts, in good yields and purities, without physically transferring hydroxide ions through the membrane. The process requires only simple extraction equipment and utilises NaOH, the cheapest and most widely available caustic source.

Our process is based on two extraction stages. First, a concentrated aqueous solution of NaOH is contacted with a hydrophobic solvent which contains a quaternary onium halide QX (X = Cl, Br, I) and a lypophilic alcohol, ROH. The differences in lipophilicity between the alkoxide ion, RO^-, and the halide, result in the formation of QOR in the organic phase, with concurrent extraction of the halide into the aqueous phase [eqns. (1) and (2)].

$$NaOH_{(aq)} + ROH_{(org)} \xrightarrow{K_1} NaOR_{(int)} + H_2O_{(aq)} \quad (1)$$

$$NaOR_{(int)} + QX_{(org)} \xrightarrow{K_2} NaX_{(aq)} + QOR_{(org)} \quad (2)$$

In the second stage, the phases are separated, and the organic phase is contacted with an aqueous solution of the appropriate alkali (or alkali-earth or quaternary onium) halide salt. The basicity potential is extracted into the aqueous phase as the QOR moiety reacts with the *water* and MX to form ROH and QX in the organic phase and MOH in the aqueous phase [eqn. (3)]. The organic phase is then recycled, with no further treatment, back to stage 1.

$$QOR_{(org)} + MX_{(aq)} + H_2O \xrightarrow{K_3} QX_{(org)} + ROH_{(org)} + MOH_{(aq)} \quad (3)$$
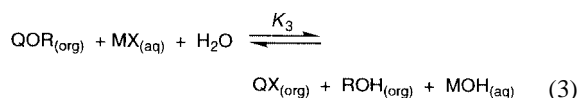
Successive extractions increase OH^-/X^- ratios in the product solution after each pass, depending on the total equilibrium constant for the above reactions (*i.e.* the extraction

Table 1 Two-stage hydroxide extraction under various conditions[a]

Entry	Parameter changed	KOH formed (% per cycle)	Extractant capacity (% per cycle)[b]	NaOH used (% per cycle)
Alcohol				
1[c]	Hexan-1-ol	4.5	18.0	0.6
2[c]	Octan-2-ol	2.5	10.0	0.5
3[c]	Pentan-2-ol	2.5	10.0	0.5
Aliquat 336 concentration[d]				
4[e]	0.5 mol kg⁻¹	4.5	18.0	0.6
5[e]	1 mol kg⁻¹	7.7	15.0	1.5
6[e]	1.5 mol kg⁻¹	13.2	17.3	2.6
Alcohol				
7	Hexan-1-ol	7.7	15.0	1.5
8	Octan-2-ol	4.5	11.0	1.1
9	None	4.1	8.0	0.8
NaOH concentration				
10[d,e]	10 mol kg⁻¹	4.5	18.0	0.6
11[d,e]	10 mol kg⁻¹	4.6	18.0	0.7
12[e]	10 mol kg⁻¹	7.7	15.0	1.5
13[e]	12.5 mol kg⁻¹	8.5	17.0	1.4
Alcohol				
14[f]	Hexan-1-ol	8.5	17.0	1.4
15[f]	Octan-1-ol	8.6	17.0	1.4
16[f]	Pinacol	19.2	37.9	3.1
17[f]	Octanane-1,2-diol	16.4	33.0	2.6

[a] *Reaction conditions* (unless noted otherwise): 10 mol kg⁻¹ NaOH; 2 mol kg⁻¹ KCl; 1 mol kg⁻¹ extracting agent in hexane. [b] Extracted hydroxide concentration relative to the theoretical hydroxide concentration that would have been obtained if the first extraction stage [eqns. (1) and (2)] was shifted completely to the right. [c] 0.5 mol kg⁻¹ extracting agent. [d] Tricaprylmethylammonium chloride. [e] Hexan-1-ol used. [f] 12.5 mol kg⁻¹ NaOH.

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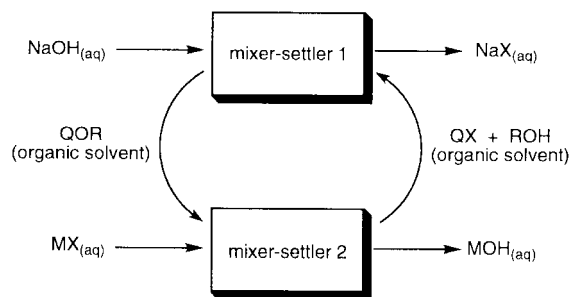
Scheme 1 Schematic representation of continuous MOH production.

is better for systems where K_1K_2 and K_3 are large). This can be explained by considering the selectivity constants§ of the various anions involved. Since the second extraction equilibrium is readily shifted to the right, the overall equilibrium constant ($K_1K_2K_3$) is determined by the selectivity constant of the alkoxide anion formed in the organic solvent. In the absence of the alcohol, the miniscule selectivity constants of the hydrophilic hydroxide anions lead to the relatively poor basicity extraction during the first extraction stage. However, the much higher selectivity constants of the alkoxide anions enhance the desired basicity extraction into the organic phase.[9,10]

The synthesis of KOH from KCl and NaOH, using different extracting agents, was chosen as a typical case study.¶ The results of extraction experiments under various conditions are summarized in Table 1. Repeated experiments showed that good yields of KOH were obtained from KCl using this method. 6–8 cycles were typically required to reach equilibrium. CsOH, LiOH and NMe$_4$OH, were similarly prepared from the corresponding chloride salts. Ammonium salt losses were typically <2% after 20 cycles, depending on solvent and concentration.

It can be seen that the extraction efficacy depends on the type of alcohol, in the order diols > primary alcohols > secondary alcohols. The high activity of diols may be attributed to possible formation of an intramolecular hydrogen-bonded complex.[10]

In conclusion, we present here a novel concept for the preparation of hydroxide salts, which is effected through a series of simple liquid anion exchange extractions. This concept may be conveniently adapted into a continuous process using mixer-settler techniques, as shown in Scheme 1, and may therefore constitute a practicable, cheap, and eco-friendly alternative to existing mercury-cell technologies.

Notes and references

‡ Lipophilic ammonium hydroxides (with at least two alkyl chains above C_8) may be obtained by extraction of hydroxide ions into an alcohol organic phase with lipophilic ammonium chlorides.[11] However, this method cannot be used for the manufacture of hydrophilic ammonium hydroxides.

§ For a given pair of anions Y^- and Z^-, the selectivity constant, $K^{sel}_{(Z/Y)}$ is defined as the equilibrium constant for the biphasic exchange reaction $QY_{(org)} + Z^-_{(aq)} \rightleftharpoons QZ_{(org)} + Y^-_{(aq)}$, i.e. $K^{sel}_{(Z/Y)} = \{[Y^-_{(aq)}][QZ_{(org)}]\}/\{[Z^-_{(aq)}][QY_{(org)}]\}$.[12]

¶ Representative experimental procedure: a source solution **A** was prepared by dissolving 50 g of NaOH in 50 g of water (50% w/w soln, 12.5 mol kg^{-1} NaOH). An extractant solution **B** was prepared by dissolving 40 g of Aliquat-336 and 12 g of pinacol in 48 g of hexane (1 mol kg^{-1} A-336 and pinacol). A destination solution **C** was prepared by dissolving 15 g of KCl in 85 g water (15% w/w soln, 2 mol kg^{-1} KCl). Solutions **A** and **B** were contacted at 25 °C, and, following phase separation, the organic (lighter) phase **B** was contacted with solution **C** at 25 °C. The phases were separated and solution **C** was analyzed for Cl$^-$ and OH$^-$ content by volumetric titration (HNO$_3$ 0.01 mol kg^{-1} for titrating OH$^-$ ions, using phenolphthalein as indicator; AgNO$_3$ 0.05 M for titrating chloride ions, using K$_2$CrO$_4$ as indicator). After the first cycle, the KCl solution contained 20 mol% KOH. The process was repeated until analysis of the chloride content of solution **C** showed that an equilibrium was reached (ca. 80 mol% KOH after eight cycles). Evaporation and filtration of the destination solution **C** precipitated the remaining KCl to yield up to >98% pure KOH soln.[13]

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