ChemComm

Polyvinyl alcohol-boronate gel for sodium hydroxide extraction

Journal:	*ChemComm*
Manuscript ID	CC-COM-03-2018-002610.R1
Article Type:	Communication

Journal Name

COMMUNICATION

Polyvinyl alcohol-boronate gel for sodium hydroxide extraction

Gretchen Marie Peters,[a] Xiaodong Chi,[a] Chandler Brockman[a] and Jonathan L. Sessler*[,a]

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Gels formed from commercially available polyvinyl alcohol (PVA) and 1,4-benzene diboronic acid (BdBA) in DMSO absorb NaOH efficiently from a bulk aqueous solution decreasing its pH.

Maintaining and manipulating the pH of an aqueous solution is a fundamental part of chemistry and biology alike. In a laboratory setting, pH is generally altered by adding an acid or base to the bulk solution. While this is a straightforward and efficient method, it also results in an increase in the concentration of extraneous ions, in the overall solution volume and in the effective mass. Thus, in certain settings, such as radioactive waste remediation, the direct addition of H^+ or OH^- may be unfavourable. Presently, there are millions of litres of legacy tank waste in the United States, and much of this waste is highly basic (pH >13; [OH^-] = 0.02 - 8.1 M).[1,2] An underlying goal of radioactive waste management and disposal is to reduce the overall amount of contaminated material. Therefore, developing ways of lowering the pH by removing the basic OH^- anions, rather than adding acid, could be advantageous. Furthermore, absorbing OH^- into a separate phase or material that could subsequently be removed would be highly attractive.

Recently, our group reported initial efforts targeting the extractive removal of the hydroxide anion. We showed that a hemispherand-strapped calix[4]pyrrole receptor could be used to decrease the pH of a bulk aqueous solution by extracting caesium hydroxide into an organic phase.[3] While success was encountered using this receptor in the context of a classic liquid-liquid extraction approach as long as the relatively hydrophobic Cs^+ counter cation was used, we envisioned that changing the receiving phase from an organic liquid to a soft material would allow for an increase in operational ease. Such a material-based approach might permit us to address the still-unmet need of direct NaOH extraction from aqueous media. With such a consideration in mind, we postulated that the combination of a diboronic acid and a diol-rich polymer would provide a system that would not only undergo gelation, but also provide the necessary binding sites for the targeted OH^- anions.

While gel formation with borax and boronic acids is well-known, these systems often require highly basic, aqueous conditions to achieve gelation.[4–7] Therefore, we turned to an organogel formed by crosslinking polyvinyl alcohol (**PVA**) with commercially available diboronic acid, 1,4-benzene diboronic acid (**BdBA**), in DMSO (Figure 1).[8] In this case, the gel network is established through the formation of trivalent boronate esters between the 1,3-diols of the **PVA** and the boronic acid units of **BdBA**. We considered this system particularly attractive because the boron centres remain uncharged and would thus, in principle, be available for hydroxide anion binding. This underlying design principle is shown schematically in Figure 1.

Upon mixing **BdBA** with **PVA** in DMSO, gelation is efficient; within minutes at room temperature gels are formed that are self-supporting and stiff (Figures S1 & S2). Based on rheological analyses involving various mixtures of these two components, we decided to work with gels formed from 50 mM solutions of **BdBA** in DMSO containing 5% **PVA**. This set of gels is shelf-stable and shows no visible dissolution or degradation when exposed to bulk aqueous media. Thus, we considered it likely that this material, referred to here as **BdBA**-**PVA**, would prove suitable for use in NaOH extraction experiments.

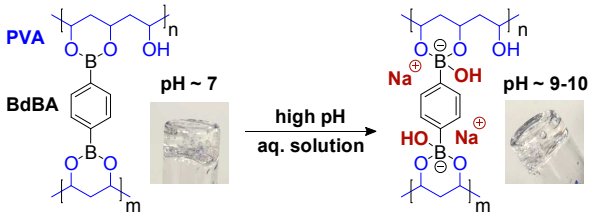


Figure 1. Gel formed with **BdBA** and **PVA** (MW = 11-31 KDa) in DMSO at r.t. (for a detailed description of gel formation, see the Supporting Information). The **BdBA** crosslinker allows for the absorption of NaOH through the formation of anionic boronate esters.

[a]*Department of Chemistry, The University of Texas at Austin, 105 E. 24th Street Stop A5300, Austin, Texas 78712-1224, United States*

†Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

To assess whether the **BdBA-PVA** gel would prove capable of absorbing NaOH, we formed the gel in a vial by combining 0.15 mL each of **PVA** (10% in DMSO) and **BdBA** (100 mM in DMSO). This produced 0.3 mL of a gel whose composition was approximately 5% in **PVA** and 50 mM in **BdBA**. A spatula was used to scrape the edges of the vial and form a "ball" of gel to maximize the surface area. We then washed this ball with H_2O to ensure that any excess **BdBA** was removed. Aqueous NaOH (1 mL, 25 mM) was then added to the vial (Figure 2A).

The pH was monitored over time by removing aliquots of the bulk aqueous solution and either directly measuring the pH using a pH probe or adding the pH-sensitive dye, phenolphthalein (**phph**), to the medium. As the pH of a basic solution decreases, **phph** undergoes a change in colour from purplish-red to clear. For these experiments, 50 µL of the bulk aqueous solution was removed and 50 µL of a 10 mM methanolic solution of **phph** was added. As can be seen from an inspection of Fig. 2A, exposure of the initial NaOH solution to the **BdBA-PVA** gel for 8 h, leads to a statistically significant decrease in the pH. Specifically, while the initial NaOH solution is dark fuchsia and has a pH of ~12.4, after 8 h of soaking, this solution is light pink in colour, and the pH has dropped to ~11.7. We quantified this colour change by UV-visible spectroscopy. Since the NaOH concentration directly correlates to the colour of **phph** (Figure S3), we used changes in the UV-vis spectral intensity at 555 nm to monitor the uptake of NaOH into the **BdBA-PVA** gel as a function of time. As shown in Figure 2B, the concentration of NaOH (25 mM at t = 0 h) in the bulk aqueous solution decreases rapidly upon exposure to the **BdBA-PVA** gel. In fact, after only 0.5 h, the pH has decreased drama-

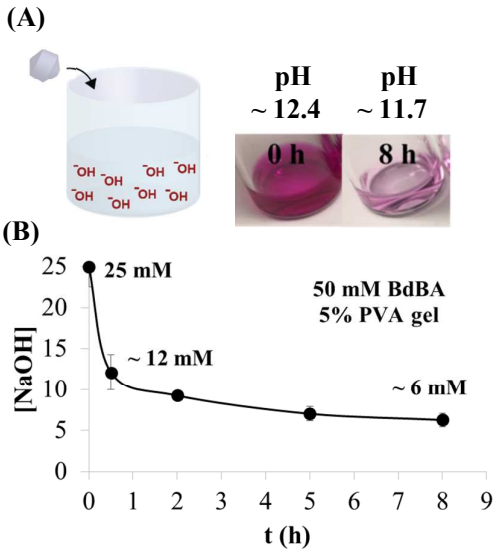


Figure 2. (A) Addition of the **BdBA-PVA** gel (0.3 mL) to a NaOH solution (1 mL, 25 mM, pH ~ 12.4), decreases the pH as shown visually by changes in the **phph** (5 mM) colour. These experiments were done by removing 50 µL from the bulk aqueous solution and adding 50 µL **phph** (10 mM in MeOH). (B) The concentration of NaOH decreases as a function of time (from 25 mM to 6 mM after 8 h). These concentrations were determined by measuring the absorbance intensity of **phph** at 555 nm as a function of time (see the experimental section in the ESI and Fig. S4).

cally, and the amount of NaOH present is less than half its original concentration. After this initial decrease, the NaOH concentration continues to drop slowly with ~75% of the NaOH being absorbed after 8 h. After 24 h, the NaOH concentration in the bulk aqueous solution was reduced to ~3.8 mM (Figure S5). Doubling the amount of the **BdBA-PVA** gel used (from 0.3 mL to 0.6 mL) resulted in 92.9 ± 0.7% NaOH absorption after only 5 h (Figure S6).

While these data are consistent with NaOH being absorbed into the **BdBA-PVA** gel, an alternative possibility is that the individual gelating components (i.e. **BdBA**, **PVA**, or DMSO) are being released into the bulk solution upon exposure to NaOH, and that this untoward release, in turn, is serving to reduce the pH. To control for this possibility, we examined each individual component and visually assessed its impact on the pH of an analogous initial NaOH solution. That is, rather than combining 0.3 mL of the **BdBA-PVA** gel to an aqueous NaOH solution (1 mL, 25 mM in NaOH), 0.3 mL of either pure DMSO, 5% **PVA** in DMSO, or 10-50 mM **BdBA** in DMSO were used instead. Again, test samples were prepared by removing 50 µL of the aqueous NaOH mixtures in question and adding 50 µL **phph** (10 mM in MeOH) as the indicator (Figure 3).

Importantly, when pure DMSO, 5% **PVA**, or a 10 mM solution of **BdBA** was used in place of the **BdBA-PVA** gel, the **phph**-containing aqueous solution remained fuchsia in colour. When 25 mM of **BdBA** was used a slight lightening of the colour was seen, indicating a subtle influence on the solution pH. The decrease in pH became notable (as inferred from the observed colour change) when 50 mM **BdBA** was mixed with the NaOH solution. Nevertheless, even in the latter instance, quantitative

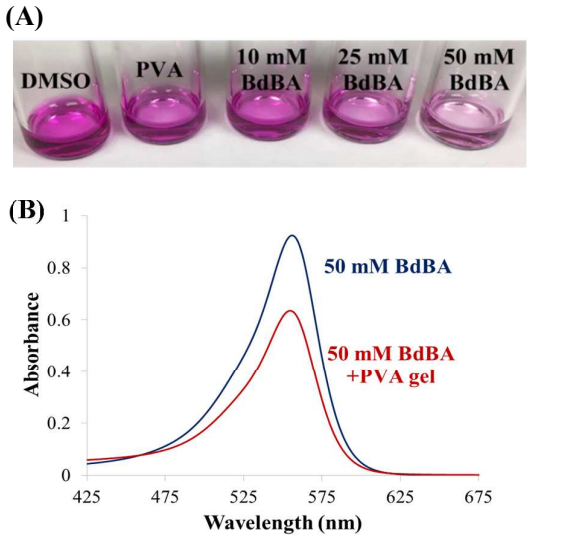


Figure 3. (A) Photographs of vials containing **phph** and aqueous NaOH with either pure DMSO, 5% **PVA** in DMSO, or 10 mM, 25 mM or 50 mM **BdBA** in DMSO, respectively. Samples were prepared by adding 0.3 mL of DMSO, **PVA** or **BdBA** at the concentrations

described to 1 mL NaOH (25 mM in H_2O). 50 µL was subsequently removed and added to a vial containing 50 µL **phph** (10 mM in MeOH). (B) UV-visible spectra of **phph** and aqueous NaOH with either **BdBA** alone (50 mM in DMSO) or the **BdBA**-**PVA** gel (50 mM, 24 h soak). Again, samples were prepared in the manner previously discussed.

UV-vis spectral analyses revealed less decrease in the pH than was obtained by allowing the gel to soak for 24 h as per the above experiments. It is also important to appreciate that to achieve a 50 mM concentration of free **BdBA** starting from the **BdBA**-**PVA** gel, 100% of the **BdBA** crosslinker would have to be released from the gel network. Since the integrity of the gel is maintained throughout the course of the experiment, we rule out mechanisms of action where the release of free **BdBA** contributes substantially to the observed pH change.

Lastly, we hypothesized that if NaOH is being absorbed into the **BdBA**-**PVA** gel, the pH inside the material should increase over the course of the experiment. To test this idea, we set-up several extraction experiments and allowed the gel to soak in aqueous NaOH (25 mM) for different lengths of time. After soaking for a specified time, the bulk aqueous NaOH solution was removed, and the vials and gels were vigorously washed with H_2O to ensure that no appreciable NaOH remained adhered to the outside of the material or free in the surrounding solution. Then, 0.1 mL of **phph** (10 mM in MeOH) was added to the remaining gel as an indicator. In each case, the **phph** was allowed to saturate the gel. Notably, we observed that the gel quickly takes up the **phph** dye.

The **BdBA**-**PVA** gels were then collected and studied at four time points (0 h, 0.25, 0.5, and 1 h) as shown in Figure 4A. While the inside of the gel is initially colourless and thus presumably neutral (t = 0 h), the longer the gel is exposed to the aqueous NaOH solution, the pinker the interior becomes. By t = 0.5 h, the **phph** inside the gel is slightly purple and after 1 h the gel mass is a deep fuchsia colour, as would be expected for a highly basic environment. We interpret these observations to mean that the pH of the bulk aqueous medium decreases upon exposure to the **BdBA**-**PVA** gel and that this reduction is indeed due to the extraction and uptake of NaOH into the gel (Figure 4B).

In summary, we have shown that a **BdBA**-**PVA** gel formed in DMSO from a commercially available diboronic acid crosslinker and polyvinyl alcohol can efficiently reduce the pH of a basic aqueous solution. This neutralization is due to NaOH extraction by the **BdBA**-**PVA** gel. Mechanistically, we propose that the neutral boronate ester linkages that make up the gel network

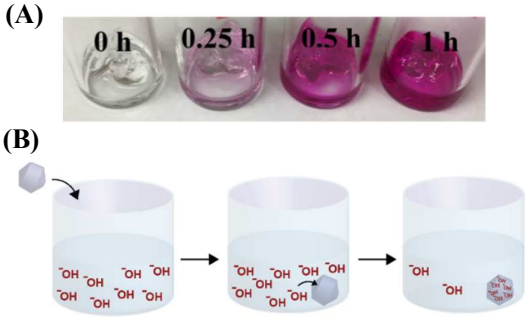


Figure 4. (A) Photos taken at different times following the addition of **phph** (0.1 mL, 10 mM in MeOH) to the **BdBA**-**PVA** gel after removal of the bulk aqueous NaOH solution. We interpret these colour changes, in concert with the other results discussed in the text proper, to mean that the **BdBA**-**PVA** gel decreases the pH by absorbing NaOH as shown schematically in (B).

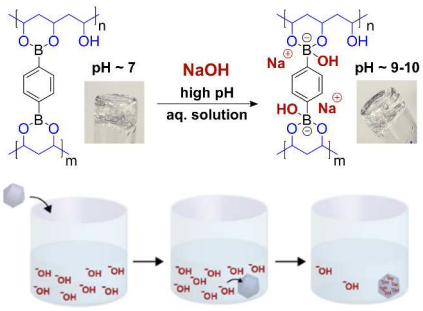
act as a binding site for OH^- anions as shown in Figure 1. Ultimately, systems such as the one described here could prove useful for reducing the pH of radioactive wastes or see application in other areas where adding further mass (e.g., a protic acid) to a reaction environment is impractical or otherwise contraindicated. More broadly, the present findings contribute to ongoing efforts to create gel systems that may be used to remove anionic pollutants from aqueous environments.[9–11]

This work was supported by U.S. Department of Energy, Office of Basic Energy Sciences (grant DE–FG02–01ER15186 to J.L.S.) and the Robert A. Welch Foundation (F-0018 to J.L.S.). Funding from the NIH 1K12GM102745 (fellowship to G. M. P.) is also acknowledged.

ORCID
Gretchen Marie Peters: 0000-0002-3634-3182
Xiaodong Chi: 0000-0002-6726-8584
Chandler Brockman: 0000-0003-1773-4601
Jonathan L. Sessler: 0000–0002–9576–1325

References

1 C. H. Delegard and S. A. Jones, *Chemical Disposition of Plutonium in Hanford Site Tank Wastes*, PNNL-23468 Rev. 1, WTP-RPT-234 Rev. 1. Pacific Northwest National Laboratory, Richland, Washington, 2015.
2 G. J. Lumetta, in *Fundamentals and Applications of Anion Separations*, eds. B. A. Moyer and R. P. Singh, Springer US, Boston, MA, 2004, pp. 107–114.
3 Q. He, G. M. Peters, V. M. Lynch and J. L. Sessler, *Angew. Chem. Int. Ed.*, 2017, **56**, 13396–13400.
4 E. Z. Casassa, A. M. Sarquis and C. H. Van Dyke, *J. Chem. Educ.*, 1986, **63**, 57–60.
5 Y. Guan and Y. Zhang, *Chem. Soc. Rev.*, 2013, **42**, 8106–8121.
6 Y. Kubo, R. Nishiyabu and T. D. James, *Chem. Commun.*, 2015, **51**, 2005–2020.
7 W. L. A. Brooks and B. S. Sumerlin, *Chem. Rev.*, 2016, **116**, 1375–1397.
8 R. Nishiyabu, H. Kobayashi and Y. Kubo, *RSC Adv.*, 2012, **2**, 6555–6561.
9 X. Ji, R.-T. Wu, L. Long, C. Guo, N. M. Khashab, F. Huang and J. L. Sessler, *J. Am. Chem. Soc.*, 2018, **140**, 2777–2780.
10 T. N. Plank, L. P. Skala and J. T. Davis, *Chem. Commun.*, 2017, **53**, 6235–6238.
11 B. O. Okesola and D. K. Smith, *Chem. Soc. Rev.*, 2016, **45**, 4226–4251.


pH ~ 7
NaOH
high pH
aq. solution
pH ~ 9-10