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# Aggregation and Capacity Limiting Effects in Anthraquinone-Based Flow Battery Negolytes

# Alexandros Pasadakis-Kavounis, Vanessa Baj, and Johan Hjelm<sup>\*,2</sup>

Department of Energy Conversion and Storage, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

Anthraquinone-based molecules are promising electroactive materials for use in aqueous organic flow batteries. At high concentrations in aqueous solutions, the well-known negolyte molecule anthraquinone disulfonic acid (AQDS) molecule has been observed to aggregate under near-neutral and acidic conditions. Aggregation has been hypothesized to be directly linked to observed concurrent capacity reduction. In this study, we investigated three different water-soluble anthraquinones in electrolytes of varying compositions and pH to gain further insight into the possible causes of capacity loss. We used low-field benchtop <sup>1</sup>H-NMR and diffusion NMR measurements directly in non-deuterated aqueous flow-battery electrolytes to investigate molecular aggregation. Single-cell testing was performed under exhaustive electrolysis conditions to determine the number of electrons exchanged per molecule. We observed a decrease in the number of electrons exchanged per molecule in the presence of carbonate ions due to  $CO_2$  adduct formation. The aggregation of the oxidized form of all three molecules studied here occurs under near-neutral and aklaine conditions and does not affect the number of accessible e<sup>-</sup>.

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#### List of Symbols

- Dmeas Apparent diffusion coefficient
- *D<sub>j</sub>* Predicted diffusion coefficient of polyaggregate formed by *j* number of monomers
- $C_0$  Total concentration
- $\vec{C}$  Concentration of polyaggregate
- *j* Number of monomers
- $K_{i,D}$  Aggregation constant calculated from change in the apparent diffusion coefficient with concentration
- $K_{i,\delta}$  Aggregation constant calculated from change in chemical shift with concentration

Anthraquinone-based molecules constitute a class of electroactive compounds with many potential applications, including as active materials in aqueous organic Redox Flow Batteries (RFBs).<sup>1-3</sup> Aqueous RFBs are attractive for large-scale and longduration energy storage owing to their nonflammable electrolytes, relatively low environmental impact, and inherent decoupling of power and energy. Such technology is needed to facilitate the integration of fluctuating renewable energy sources into the power grid.<sup>4-6</sup> The use of anthraquinones as active materials offers great chemical tunability.<sup>7</sup> The insertion of charged side groups, such as sulfonates or phosphonate groups, increases solubility and leads to higher energy densities. Substituents attached to the redox-active core, as well as the oxidation state of the core, can strongly influence the aggregation behavior of redox-active aromatic organic molecules.<sup>8</sup> In particular, water-soluble anthraquinone derivatives have been intensively studied as active materials in redox-flow battery electrolytes.<sup>9,10</sup> Carney et al. investigated acidic and mildly alkaline buffered 9,10-anthraquinone-2,7-disulfonic acid (AQDS) electrolytes and showed that aggregation is simultaneously accompanied by a reduction in the achievable capacity or the number of electrons exchanged per molecule,<sup>11</sup> Carney et al. linked the capacity reduction to dimer formation. A CO<sub>2</sub> adduct with AQDS hydrolyzes in solution to semi-anthraquinone and a carbonate ion. Subsequently, two semi-anthraquinones disproportionate to form fully oxidized AQDS and dihydroanthraquinone. The two species

then dimerize to yield either 1  $e^-$  (mildly alkaline pH) or 1.5  $e^-$  (acidic pH), depending on the pH of the solution.<sup>11</sup>

We set out to study the aggregation of three different watersoluble anthraquinone molecules in non-deuterated solutions to better understand the effect of pH, electrolyte composition, and substituents on the aggregation, and to investigate possible correlations with the achievable capacity. The aggregation of AQDS has been previously studied in deuterated media using concentrationdependent chemical shifts<sup>11</sup> and diffusion NMR.<sup>12</sup> Since hydrogen bonding probably plays an important role in the aggregation of water-soluble organic materials, the aggregation constants measured in deuterated water may not accurately reflect aggregation in aqueous electrolytes.<sup>13</sup> The use of <sup>1</sup>H-NMR with solvent suppression allows direct monitoring of organic molecules in aqueous flow battery electrolytes. Here we employed low-field benchtop <sup>1</sup>H-NMR spectroscopy with solvent suppression and pulsed-field gradient spin echo experiments (PGSTR) to determine concentration-dependent chemical shifts and apparent diffusion coefficients of the monomer and formed aggregates (e.g. dimers) in aqueous electrolytes, and compare the results of the two methods. It is well established in literature how to calculate diffusion coefficients from cyclic voltammetry<sup>14</sup> or NMR spectroscopy,<sup>15</sup> but it is still a complicated issue to differentiate among multiple diffusion coefficients in the presence of more than one species (in this case monomer and dimer) unless the species have well separated redox waves and/or well separated peaks in the NMR.<sup>16,17</sup>

#### Experimental

All chemicals were purchased from commercial suppliers (Sigma-Aldrich, TCI Chemicals, Fluorochem, and VWR Chemicals) and used without further purification. Single-cell testing was performed using commercial cell test hardware from Fuel Cell Technologies. The cell consisted of a Fumasep E-630(K) membrane (Fumatech BWT GmbH) sandwiched between two pieces of AvCarb carbon cloth. The active area was taken as the geometric area of the electrodes and was 5 cm<sup>2</sup>. The electrode/membrane assembly was sandwiched between two carbon polymer composite plates with integrated serpentine flow fields, followed by current collectors and end plates, resulting in a zero-gap cell configuration. The carbon cloths were thermally activated by heat treatment in air at 400 °C for





**Figure 1.** Number of electrons accessed in single-cell tests of AQDS negolytes of different electrolyte compositions, paired with  $K_4[Fe(CN)_6]$  for a and  $Na_4[Fe(CN)_6]$  for (b) and (c). The capacity of the posolyte was twice as high as the negolyte making the latter the capacity limiting side in all tests. (a) AQDS (33 mM) was dissolved in 0.26 M KH<sub>2</sub>PO<sub>4</sub> and 0.75 M KCl, and the pH of the electrolyte was 7.35. The current density used was 5 mA cm<sup>-2</sup>, and a cycle lasted 2 h. The theoretical and experimental capacities were 25 mAh and 23 mAh, respectively. b) 10 mM AQDS was dissolved in 0.5 M NaHCO<sub>3</sub> with a pH of 8.5. The current density used was 1 mA cm<sup>-2</sup> and one cycle lasted 1.3 h. The theoretical and experimental capacities were 5.36 mAh and 3.51 mAh, respectively. (c) AQDS (50 mM) was dissolved in 1 M NaOH. The current density used was 10 mA cm<sup>-2</sup> and one cycle lasted 1 h. The theoretical and experimentally observed capacities were 26.8 mAh and 25.3 mAh, respectively.

24 h prior to use. The membrane was used as supplied, without any pretreatment. A constant current protocol with low current density was used to minimize ohmic losses and utilize all available capacity, similar to exhaustive bulk electrolysis. Sodium or potassium ferrocyanide was used as the posolyte in all cases. The theoretical capacity of the posolyte was twice that of the negolyte, making the latter the capacity limiting side in all cases.<sup>18</sup> Cycling voltammetry was performed using a three electrode setup with a glassy carbon disk as working electrode, Pt wire as counter electrode and a leakfree Ag/AgCl electrode (3.4 mol  $l^{-1}$  KCl) purchased from eDAQ as a reference. Prior to any measurements, the solutions were purged for 10 min either by Ar or by CO<sub>2</sub>. Hereafter, a blanket of Ar or CO<sub>2</sub> was maintained over the solution to prevent any oxygen from redissolving in the solutions. <sup>1</sup>H-NMR spectra and PGSTE measurements were recorded on a Magritek Spinsolve spectrometer, operating at 80 MHz (<sup>1</sup>H). Unless specified otherwise, all spectra were acquired at room temperature  $(22.8 \pm 0.15)$  and referenced to the main internal solvent residue, which was water (4.79 ppm). Eight <sup>1</sup>H pulsed gradient stimulated echo (PGSTE) NMR ( $\Delta = 0.2$  s,  $\delta =$ 3 ms) spectra with varied square gradient field amplitudes (g =32.25, 79.00, 107.0, 129.0, 147.8, 164.4, 179.6 or 193.5 mT m<sup>-1</sup>) were acquired for each sample. Diffusion coefficients were then calculated by fitting the intensities observed to the Stejskal-Tanner equation<sup>19</sup> using the GNAT<sup>20</sup> software package.

#### Results

This study focuses on three water-soluble anthraquinones; sodium-2,7-anthraquinone disulfonate (AQDS), 2,6-dihydroxyanthraquinone (DHAQ), and 4,4'-[(9,10-Dioxo-9,10-dihydroanthracene-2,6-diyl)bis(oxy)]dibutyric acid (DBEAQ). The introduction of water-soluble groups, such as hydroxyl groups, as in the case of 2,6-dihydroxyanthracene-9,10-dione (DHAQ), has been shown to increase the solubility of the core structure in aqueous media.<sup>21</sup> The  $pK_a$  of phenol-like groups is around 10,<sup>22</sup> which leads to practically complete deprotonation at pH values of 13-14 and consequently makes the molecule very soluble in water. AQDS has two sulfonic acid groups, which are always present in the deprotonated form at any accessible pH value.<sup>23</sup> Solubility can be further increased using flexible side chains terminated with a solubilizing group<sup>24,25</sup> such as with 4,4'-((9,10-dioxo-9,10-dihydroanthracene-2,6-diyl)bis(oxy))dibutyric acid (DBEAQ). DBEAQ has two butyric acid chains linked to its hydrophobic anthraquinone core via an ether linkage. Since butyric acid has a pKa of 4.8, the side chains used here will have a similar pKa and are therefore deprotonated at all pH values used in this work (pH > 7).<sup>26</sup> The aqueous solubility of organic compounds is influenced by the symmetry of the molecule and the counterion.<sup>27</sup> The choice of counterion for each electrolyte was based on the solubility of the anthraquinone tested. AQDS has higher solubility in the presence of Na<sup>+</sup> ions, whereas both DHAQ and DBEAQ have higher solubility with K<sup>+</sup> ions.

Electrochemical evaluation.—The effect of pH and solubilizing substituents on the achievable capacity was determined using singlecell testing with different negolyte compositions and at near neutral and alkaline pH. The capacity recorded from the charge/discharge cycles, expressed as the number of electrons per molecule based on the theoretical capacity, is shown in Fig. 1 for AODS and Fig. 2 for DHAQ and DBEAQ. AQDS was tested with two different nearneutral electrolytes, one with phosphate (pH 7.35) and the other with carbonate (pH 8.5), to distinguish pH effects from carbonate- and/or CO<sub>2</sub>-related specific effects. In the case of the near-neutral phosphate-buffered electrolyte (Fig. 1(a)) and the alkaline electrolyte (Fig. 1(c)), almost two (1.8 and 1.9) electrons per molecule were observed, except when the supporting electrolyte was NaHCO<sub>3</sub> (Fig. 1(b)). In all cases, the first cycle showed abnormal cycling behavior, most likely due to scavenging of dissolved oxygen,<sup>11</sup> and the presence of small amounts of CO<sub>2</sub>.<sup>28</sup> Figure 3 illustrates the voltammetric traces of AQDS and DBEAQ in CO2 saturated electrolyte as well as in carbonate containing electrolyte at two different pH values. Figure 4 shows the evolution of the voltammograms of AQDS and DBEAQ in carbonate buffer as a function of pH.

To investigate the effects of other anionic substituents attached to the anthraquinone core we tested DHAQ and DBEAQ. DHAQ has two acidic protons that affect the pH of the electrolyte. When DHAQ (0.5 M) is dissolved in a solution of 2 M KOH, the final concentration of OH<sup>-</sup> due to the neutralization of the OH<sup>-</sup> ions by the release of the phenolic protons of DHAQ is 1 M. A solution of K<sub>2</sub>CO<sub>3</sub> is not sufficiently alkaline to dissolve DHAQ and therefore was not tested. To evaluate the effect of carbonate ions on the electrochemical performance of DHAQ, K<sub>2</sub>CO<sub>3</sub> was added to a 2 M KOH solution for the high concentration DHAQ test and to a 1 M KOH solution for the low concentration DHAQ test. The carboxylic protons of DBEAQ are more acidic than the phenolic protons of DHAQ, so DBEAQ could dissolve in the carbonate solution. In this case, 0.5 M NaHCO<sub>3</sub> was used as the supporting electrolyte for direct comparison with the corresponding AQDS test.



**Figure 2.** Number of electrons accessed in single-cell tests of DHAQ and DBEAQ negolytes paired with  $K_4$ [Fe(CN)<sub>6</sub>] posolyte. The capacity of the posolyte was twice as much as the negolyte making the latter the capacity limiting side in all tests. (a) 500 mM DHAQ was dissolved in 2 M KOH. The current density used was 50 mA cm<sup>-2</sup> and a complete cycle lasted 2 h. The theoretical and experimental capacities were 268 mAh and 255.8 mAh, respectively. (b) DHAQ (250 mM) was dissolved in 2 M KOH with 0.25 M K<sub>2</sub>CO<sub>3</sub>. The current density used was 20 mA cm<sup>-2</sup> and a complete cycle lasted 3.3 h. The theoretical and experimental capacities were 201 mAh and 169.81 mAh, respectively. (c) DHAQ (10 mM) was dissolved in 1 M KOH with 0.5 M K<sub>2</sub>CO<sub>3</sub>. The current density were 5.36 mAh and 5.6 mAh, respectively. (d) 10 mM DBEAQ was dissolved in 0.5 M NaHCO<sub>3</sub>. The current density used was 1 mA cm<sup>-2</sup> and one cycle lasted 2 h. The theoretical and experimental capacities were 5.36 mAh and 5.6 mAh, respectively. (d) 10 mM DBEAQ was dissolved in 0.5 M NaHCO<sub>3</sub>. The current density used was 1 mA cm<sup>-2</sup> and one cycle lasted 2 h. The theoretical and experimental capacities were 5.36 mAh and 5.6 mAh, respectively. (d) 10 mM DBEAQ was dissolved in 0.5 M NaHCO<sub>3</sub>. The current density used was 1 mA cm<sup>-2</sup> and one cycle lasted 2 h. The theoretical and experimental capacities were 5.36 mAh and 5.6 mAh, respectively.

*NMR investigation.*—It is known that organic molecules with an anthracene core self-associate in polar solvents by  $\pi$ -stacking interactions.<sup>29,30</sup> In the case of DHAQ, AQDS and DBEAQ, the quinone functional group can also actively participate in the aggregation process by forming hydrogen bonds.<sup>11</sup> H-NMR spectroscopy can be used to determine aggregation constants ( $K_{agg.,\delta}$ ) and provides information about the structures of the aggregates.<sup>31</sup> The equilibrium between monomeric species and aggregates is fast compared to the NMR time scale.<sup>32</sup> Thus, a change in the chemical shift ( $\delta$ ) of the proton signals is observed in the NMR spectra by varying the concentration, which is the weighted average of all species (monomers and polyaggregates) present in the solution. Further information about the structure of the aggregates could be gained by studying the concentration-dependent change in the chemical shift ( $\Delta\delta$ ) of the different protons in the three molecules. AQDS was examined in both 0.5 M NaHCO<sub>3</sub> (Fig. S1, supporting information) and 1 M NaOH (Fig. S2). DHAQ was studied in 1 M KOH (Fig. S3), 2 M KOH

(Fig. S4, and 2 M KOH containing 0.5 M K<sub>2</sub>CO<sub>3</sub> (Fig. S5). Finally, DBEAQ was analyzed in 1 M KOH (Fig. S6). <sup>1</sup>H-NMR measurements were performed at various dilutions. In the titration of DHAQ, all three aromatic protons were upshielded and broadened when the concentration was increased. This behavior is typical of aromatic  $\pi$ -stacks and is the result of the mutual shielding of two closely spaced aromatic rings.<sup>33</sup> Notably the  $\Delta\delta$  of the two protons next to the quinone moiety are almost twice as high (0.439 and 0.339 ppm) as that of the third proton (0.238 ppm). If the interaction was a pure  $\pi$ -stacking, the  $\Delta\delta$  of the three protons should be similar since they would be equally affected. There could also be counter-ion bonding and/or direct or solvent-mediated hydrogen bonding between the carbonyls belonging to the quinone systems, as well as between hydrophilic substituents on adjacent monomers.

A similar titration of AQDS has already been performed by Carney et al. in deuterated solvents at different pH values ( $D_2O$  and DMSO- $d_6$ ).<sup>11</sup> Here we performed a titration of AQDS in 1 M NaOH,



**Figure 3.** Cyclic voltammograms of AQDS (*top*) and DBEAQ (*bottom*) at 0.5 M NaHCO<sub>3</sub> (red figures) 0.5 M NaCl (blue figures). Two different pH values are shown for the NaHCO<sub>3</sub> solutions, one at the starting solutions with no acidification (solid line) and the other at the lowest pH value (dotted line). Acidification took place by slow addition of 1 M HCl solution. Meanwhile, in the case of the NaCl solutions the solid lines present the voltammograms recorded under Ar atmosphere while the dotted lines present the voltammograms recorded under CO<sub>2</sub>.

where the capacity was 1.9 electrons per molecule, and in 0.5 M NaHCO<sub>3</sub>, where the observed capacity corresponded to only about 1 electron per molecule. The aromatic <sup>1</sup>H-NMR signals showed the same concentration dependence as for DHAQ. Also, for AQDS and DBEAQ, the  $\Delta\delta$  of the two protons adjacent to the quinone unit was larger than for the other protons. In addition, the protons of the side chain right next to the oxygen were upshielded, whereas the other two protons of the side chain were not affected as much by the variation of concentration (Fig. S6, Supporting Information). In the case of  $\pi$ -stacking, the shift of the protons outside the aromatic ring should be in the opposite direction because they would be affected by de-shielding phenomena.<sup>33</sup> This indicates that the primary aggregation-related intermolecular interaction in anthraquinone systems is hydrogen/ counter ion bonding, in the absence of carbonate.

The chemical shifts and apparent diffusion coefficients at different concentrations for the relevant protons were registered for each molecule and the  $K_{i,\delta}$  (Aggregation constant using the chemical shifts) and the  $K_{i,0}$  (Aggregation constant using the change in diffusion coefficient with concentration) (Section 3.1, Supporting Info) were determined using nonlinear regression and an isodesmic model.<sup>11,34,35</sup> Figure 5 shows the chemical shift as a function of concentration with the fitted isodesmic model. The isodesmic model assumes that the aggregation constant is the same for all possible polyaggregates.<sup>12</sup>



**Figure 4.** Cyclic voltammograms of AQDS (*top*) and DBEAQ (*bottom*) at 0.5 M NaHCO<sub>3</sub> slowly acidified with 1 M HCl resulting in different pH values. The arrow shows the difference between the expected oxidation peak, from the new oxidation peak caused by binding of  $CO_2$  on the quinone moiety.

$$A + A \to A_2 \quad K$$

$$A_2 + A \to A_3 \quad K$$

$$nA \to A_n \quad K_i = K^n \tag{1}$$

The obtained best-fit values after fitting the model to the data are tabulated below (Table I).

**Diffusion NMR.**—At each concentration, a Pulse Gradient Stimulated Echo (PGSTE) was performed to measure the trend of the diffusion coefficient with concentration. Similarly, an Isodesmic model (Eq. 2) was used to fit the observed diffusion coefficient, as described by Ferrazza et al.<sup>34</sup>

$$D_{meas} = D_m \frac{C}{C_0} \sum_j j^{\frac{2}{3}} (K_{i,D}C)^{j-1}$$
[2]

Where  $D_{meas}$  is the apparent diffusion coefficient,  $C_0$  and C are the total concentration of anthraquinone and the concentration of polyaggregate, respectively. *j* is the number of monomers and  $K_{i,D}$  is the aggregation constant resulting from the change of the apparent diffusion coefficient with concentration. The measured diffusion coefficients were corrected for the increased viscosity by monitoring the change of diffusion coefficient of the water peak (S3, Supporting Info).<sup>17,36</sup> The apparent diffusion coefficients corrected for viscosity at each concentration, alongside the Isodesmic best-fit model line, are displayed in Fig. 6.

#### Discussion

AQDS showed an electrolyte utilization corresponding to  $2 e^{-}$  in both neutral-pH-phosphate and alkaline electrolyte (Figs. 1(a) and 1(c)). This shows that the observed capacity at a pH of >7 in the absence of carbonate/CO<sub>2</sub> is not strongly affected by pH. When



Figure 5. The observed chemical shift (scatter points) with the fitted isodesmic model (lines) of the three anthraquinones in different electrolytes. (a) The perturbation of the chemical shift of DHAQ in 1 M KOH (red), 2 M KOH (green), and 2 M KOH/0.5 M K<sub>2</sub>CO<sub>3</sub> (blue). (b) The chemical shift of an aromatic proton (black) and an aliphatic proton (yellow) of DBEAQ in 1 M KOH. (c) The chemical shift of AQDS in 1 M NaOH (cyan) and 0.5 M NaHCO<sub>3</sub> (purple).

Table I. Aggregation constants of the three molecules studied (DHAQ, AQDS, and DBEAQ). The last line indicates the number of species assumed in the Isodesmic model describing the change of diffusion coefficient with concentration, as shown in Eq. 2.

	DHAQ			AQDS		DBEAQ
	1 M KOH	2 M KOH	2 M KOH, 0.5 M K <sub>2</sub> CO <sub>3</sub>	1 M NaOH	0.5 M NaHCO <sub>3</sub>	1 M KOH
$K_{i,\delta}$ (L/mol)	20.1 ± 7.8	$9.3 \pm 0.5$	$1.27 \pm 0.2$	$5.34 \pm 0.2$	3.14 ± 1.9	$10.7 \pm 5.2$
$K_{i,D}$ (L/mol)	$16.3 \pm 4.9$	$10.5 \pm 1.6$	$2.09 \pm 0.5$	$4.22 \pm 0.4$	$2.98 \pm 0.3$	$8.41 \pm 0.9$
Number of monomers for $K_{i,D}$	12	5	2	2	2	2

AQDS was dissolved in 0.5 M NaHCO<sub>3</sub> solution, we observed about 1.25 electrons per molecule in the first cycle, decreasing to one electron per molecule in the following cycles, which is similar observations to the work of Carney et al.<sup>11</sup>Both DBEAQ and DHAQ have shown an almost full 2 e<sup>-</sup> capacity in KOH solutions.<sup>37</sup> When carbonate ions are present in such alkaline solutions, the number of e<sup>-</sup> used for DHAQ is slightly reduced but to a lesser extent than AQDS. Meanwhile DBEAQ remains unaffected, indicating that capacity limiting effect of carbonate is a molecule-solute specific interaction.

In order to gain more insight as to why AQDS is affected more strongly by  $CO_3^{2-}$  than DBEAQ, we performed a series of cyclic voltammetry experiments (CV) at different pH values. The starting solution was 0.5 M NaHCO<sub>3</sub>, which was subsequently slowly acidified with 1 M HCl. Additionally, CVs in Ar or CO<sub>2</sub> saturated electrolytes for both AQDS and DBEAQ were recorded in order to assess the effect of CO<sub>2</sub> on these molecules. The resulting voltammograms are shown in Figs. 3 and 4.

CO2 has been shown to bind on the hydroxyl moiety of hydroquinones, forming a CO<sub>2</sub> adduct, and altering the electrochemical response of the quinone.<sup>38</sup> In the case of AQDS and DBEAQ the concerted two-electron re-oxidation process that is normally seen in aqueous electrolyte, splits into two distinct one electron oxidation steps when the solution is purged with CO<sub>2</sub> (Fig. 3, blue plots). Carbonate and bicarbonate ions are in equilibrium with CO<sub>2</sub> in solution yielding an increasing amount of CO<sub>2</sub> when the pH approaches or dips below the pKa value of  $HCO_3^{-1}$ (pKa = 8.2)<sup>38</sup> The effect of the formation of CO<sub>2</sub> during the acidification of the carbonate solution and subsequent binding to the anthraquinone can be seen on the red voltammetric traces in Fig. 3. In the case of 0.5 M NaHCO<sub>3</sub> solution at pH = 9.5 the resulting voltammograms look similar to those recorded at 0.5 M NaCl under Ar atmosphere, reflecting the relatively low concentration of CO<sub>2</sub> generated from the carbonate present in solution at this pH. When the pH of the carbonate solution is decreased further, the resulting voltammograms become similar to those recorded in CO<sub>2</sub> saturated electrolyte. The evolution of the voltammograms as a function of pH

can be seen in Fig. 4 for both AQDS and DBEAQ. The separation of the first and second oxidation peak (indicated by an arrow on Fig. 4) reflects the binding strength of  $CO_2$  on the hydroquinone moiety.<sup>38</sup> The results indicate that  $CO_2$  forms a stronger bond with AQDS than DBEAQ, reflected in the greater shift of the second one-electron reoxidation process for AQDS than for DBEAQ.

The potential of the second oxidation step of AQDS is 0.24 V vs SHE. The redox potential of ferro-/ferri-cyanide, that AQDS was paired with, is 0.48 V vs SHE.<sup>39</sup> As such, in order to access the second oxidation step in a full battery consisting of AQDS and  $K_4$ [Fe(CN)<sub>6</sub>] in a CO<sub>2</sub>-containing electolyte the lower potential limit in a full cell cycling test should be less than 0.24 V (Fig. S7). The cut-off potential in Fig. 1b were set to 0.4 V–1 V. As such, any AQDS-CO<sub>2</sub> adduct formed in operando by pH swing during charging would not be fully oxidized during discharge leading to a decreased apparent number of electrons.

The observed concentration dependent chemical shift and apparent diffusion coefficient indicates that aggregation takes place. The aggregation constant and the predicted changes in calculated from Eq. 2 may vary depending on the number of monomers considered (*j*). Therefore, 4 different numbers of monomers forming the polyaggregate were tested when Eq. 2 was fitted to the experimental data (Fig. 6). In the case of AQDS and DBEAQ, the shape of the line was not affected by the number of species.  $K_{i,D}$  values agree with  $K_{i,\delta}$  when dimers are considered as the primary aggregation species. Higher aggregates were observed only for DHAQ in 1 M and 2 M KOH solutions. DHAQ displays the highest aggregation constant, and aggregation numbers of 12 and 5 monomers, in the absence of carbonate. Compared to DBEAQ and AQDS, DHAQ does not carry the bulky sulfonate side groups of AQDS or the long flexible chains of DBEAQ which may hinder aggregation.

The observed apparent diffusion coefficient suggests the formation of polyaggregates larger than dimers. This is based on the predicted change in the diffusion coefficient  $(D_j)$  with increasing aggregation number (j) when spherical aggregates are assumed and the Stokes-Einstein equation is applied, as proposed by Ferrazza et al.<sup>34</sup> (Eq. 3).



**Figure 6.** Diffusion coefficient of AQDS (red) in 1 M NaOH (a) and 0.5 M NaHCO<sub>3</sub> (b), DBEAQ (green) in 1 M KOH (c), and DHAQ (blue) in 2 M KOH (d), in 1 M KOH (e), and 2 M KOH / 0.5 M K<sub>2</sub>CO<sub>3</sub> (f) as a function of concentration. The dotted lines represent the best fit of the isodesmic model with four different numbers of monomers forming the main polyaggregate. The gray lines represent the diffusion coefficient calculated using Eq. 3 for polyaggregates with different numbers of monomers.

$$D_j = \frac{D_m}{j^{\frac{1}{3}}}$$
[3]

Interpretation of the observed changes in the diffusion coefficient using this model suggests that aggregates of 7–10, 16, and 3–8 molecules form for AQDS, DBEAQ, and DHAQ, respectively. The assumption of spherical aggregates may not be a very accurate model for the aggregates formed here, but it is likely an indication that a distribution of polyaggregates larger than dimers is formed.

#### Conclusions

In this work, we investigated the effects of pH, electrolyte composition, and solubilizing side group on the accessible capacity and the effects on aggregation of three model molecules based on a hydrophobic anthraquinone core modified with different charged solubilizing groups, in non-deuterated electrolytes. We observe a capacity of approximately 2 e-/mol AQDS in mild-alkaline phosphate-buffered solution when cycled between 0.4-1.0 V, while only 1 e<sup>-</sup> / mol is observed in carbonate-buffered mild-alkaline electrolyte using the same cut-off potentials. We attribute this to the adductformation of CO2 with AQDS which causes the re-oxidation process of AQDS to split in two separate 1-electron steps. The second electron step is at a significantly more positive potential, which lies outside of the potential range accessed during battery operation. This leads to incomplete discharge of AQDS that is registered as reduced capacity in our cycling experiments. In alkaline medium, all three molecules yield 1.8-1.9 e-/mol in the absence of carbonate ions and only a slight decrease in the capacity of DHAQ in the presence of carbonate. DBEAQ was not significantly affected by carbonate under similar conditions, which agrees with the weaker interaction of this molecule with CO<sub>2</sub>, reflected in a smaller peak separation between the consecutive 1-electron re-oxidation processes observed in the voltammetry. Thus, the nature of the substituents on the anthraquinone affects the sensitivity to carbonate. The aggregation study performed here was carried out with the oxidized form of anthraquinone and showed aggregation of all three molecules in all media studied, with aggregation constants of the same order of magnitude. Aggregation in the oxidized state alone is not a good indicator of capacity-limiting effects, and we have found no correlation between aggregation and capacity reduction. The results of this study suggest that controlling specific interactions with electrolyte components is more important than preventing aggregation for developing electrolytes with high capacity utilization. Control of aggregation of redox-active organic molecules can still be considered an additional parameter in the design of flow battery electrolytes. While also other aqueous organic systems exhibit full capacity utilization despite strong aggregation<sup>40</sup> it is possible that that aggregates may exhibit beneficial microenvironmental effects<sup>41,42</sup> and influence mass transfer losses and cross-over properties via the decreased diffusion coefficient and increased hydrodynamic radius.

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## ORCID

Johan Hjelm (1) https://orcid.org/0000-0003-0072-5784

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