Spectroscopic Measurement of State of Charge in Vanadium Flow Batteries with an Analytical Model of $\text{V}^{IV}-\text{V}^{V}$ Absorbance

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The ultraviolet-visible spectra of catholytes for vanadium flow batteries (VFBs) were measured and analyzed for a range of $\text{V}^{IV}$-$\text{V}^{V}$ ratios and vanadium concentrations. Using a model of $\text{V}_2\text{O}_5^{3-}$ in equilibrium with $\text{VO}^{2+}$ and $\text{VO}_2^{2+}$, the spectra were characterized in terms of an excess absorbance parameter $p$ and the molar extinction coefficients $\varepsilon_p$ and $\varepsilon_q$ of $\text{VO}^{2+}$ and $\text{VO}_2^{2+}$, respectively. The results showed that $p$ varies weakly with the vanadium concentration $C$ and this variation was quantified relative to a reference concentration $C_R$ by means of a concentration coefficient $\phi_p$. Experimental data showed that plots of $\phi_p$ versus $C$ and plots of $1/\varepsilon_q$ versus $C$ are linear and, based on this linearity, $\phi_p$ was expressed as a simple function of $C$ in terms of its reference concentration $C_R$ and a single parameter $M$ that is independent of the choice of $C_R$. Standard spectra of $p$ at a concentration $C_R = 1 \text{ mol dm}^{-3}$ and of $\varepsilon_p$ and $\varepsilon_q$ were generated from which the spectrum of any catholyte may be simulated using the measured value of $M$ in a governing equation. This enables determination of the state of charge for any VFB catholyte using absorbance measurements at a small number of wavelengths.

The use of non-dispatchable power sources such as solar, wind and ocean energy is increasing.1 Due to the intermittency of these sources, their use is restricted unless there is a means of storing the energy they produce in periods of high availability for utilization in periods of limited availability.2,3 There is considerable interest in flow batteries for storing energy from such sources and for other large and medium scale energy storage applications.4,5 Vanadium flow batteries (VFBs),6–13 also known as vanadium redox flow batteries (VRB or VRB), are particularly attractive because, in addition to having long cycle life, they are essentially immune to cross-contamination problems due to mass transfer across the membrane that can limit the service life of the electrolyte in other systems.3,4,14–19 This is because both the positive and negative sides of a VFB are based on vanadium species, eliminating the need for costly re-purification processes.1,12 Typical cells have carbon felt electrodes; both cell design and the electrochemical behavior of electrodes are active areas of research.20–31 The cells can operate at coulombic efficiencies of over 90%32,33 and their carbon electrodes have very good stability as long as the positive half-cell is not overcharged.34,35

Accurate monitoring of state of charge (SoC) of both electrolytes is important for effective operation of flow battery technology. For example in a VFB, transfer of vanadium ions across the membrane34–36 and side reactions such as hydrogen formation33–35 at the negative electrode can cause the battery to become unbalanced (e.g. more $\text{VO}^{2+}$ on the positive side than $\text{VO}^{2+}$ on the negative), and balancing by overcharging is not practical because it can lead to significant degradation of the carbon at the positive electrode.

The principal active species in a VFB are vanadyl ($\text{VO}^{2+}$) and perravanadyl ($\text{VO}_2^{2+}$) ions (i.e. $\text{V}^{IV}$ and $\text{V}^{V}$) in the positive electrolyte (catholyte) and $\text{V}^{III}$ and $\text{V}^{IV}$ in the negative electrolyte (anolyte), typically in $\text{H}_2\text{SO}_4$ solutions. These solutions are highly colored:36–38 thus, as we have previously suggested,40,46,47,53–55 ultraviolet-visible (UV-Vis) spectroscopy offers an attractive method of independently measuring the SoC of both electrolytes.

Other methods of measuring SoC are available.56,58–65 These include monitoring of cell potentials,58,59,61,62 measurements of the potential of individual electrodes against reference electrodes36,63 and measurements of electrolyte conductivity.64–66 However, these methods have limited accuracy;67,68 e.g. it is not always simple to accurately convert potential measurements to SoC since small offsets and drifts in the potential can lead to significant error, especially for mixture ratios close to 50%. In addition, these methods, being electrochemical, do not provide readings that are truly independent of the cell output. They cannot distinguish variation due to change in mixture ratio from spurious variation due to the presence of impurities, dissolved hydrogen or oxygen or other issues that alter the behavior of the electrodes and they cannot measure the concentration of vanadium.

Spectroscopic monitoring of SoC is independent of electrochemistry and offers the possibility of performing in-situ analysis. Because the absorbance of $\text{V}^{IV}$-$\text{V}^{V}$ mixtures is a linear combination of that of the constituents, it is straightforward to implement UV-Vis spectroscopic monitoring of the SoC of the anolyte. Indeed, this technique has been used in several studies.66–68 A similar methodology can be used for very dilute $\text{V}^{IV}$-$\text{V}^{V}$ mixtures67,68 and has been used to study mass transport and the effect of side reactions within a VFB.69–72 However, at the concentrations typically used in a VFB, the absorbance of $\text{V}^{IV}$-$\text{V}^{V}$ electrolytes is high and is a very non-linear function of the mole fraction of $\text{V}^{IV}$ and of overall vanadium concentration.40,45–47,53,55–57,52 Because of this, it was previously suggested in the literature that UV-Vis spectroscopic monitoring of VFB catholytes is not feasible.64 Tang et al.52 and Liu et al.73–77 addressed the problem of non-linearity by developing an empirical method of estimating SoC by numerically comparing spectra from operating VFBs with large sets of calibration spectra. However, such methods have severe limitations because of effects such as changes in the vanadium concentration due to transfer of water and vanadium across the membrane72,78 which cause the
calibration of spectra to drift severely with each charge-discharge cycle of the battery. These problems can be avoided by careful analysis of the spectroscopic behavior of concentrated mixtures of V\textsuperscript{IV} and V\textsuperscript{V} based on the underlying solution chemistry.

There have been a number of studies of the UV-Vis spectroscopy of V\textsuperscript{IV} and V\textsuperscript{V} and their mixtures in aqueous electrolytes.\textsuperscript{45,47,53,55,57,72} We have earlier reported\textsuperscript{40,46,47,53,55–57,72} such a study of VFB electrolytes and have shown that the non-linear absorbance behavior of the catholyte can be quantitatively explained by the formation of a strongly absorbing 1:1 mixed-valence complex, V\textsubscript{2}O\textsubscript{3}\textsuperscript{3+} in equilibrium with VO\textsuperscript{2+} and VO\textsubscript{2}\textsuperscript{+}. A model of the spectra based on this equilibrium, using an excess absorbance parameter $p$ to quantify the effect of V\textsubscript{2}O\textsubscript{3}\textsuperscript{3+} formation together with the extinction coefficients of VO\textsuperscript{2+} and VO\textsubscript{2}\textsuperscript{+}, shows excellent quantitative agreement with experiment and comprehensively explains the spectroscopic behavior. Although it is difficult to determine the equilibrium constant accurately, we have reported approximate values, an approximate spectrum of V\textsubscript{2}O\textsubscript{3}\textsuperscript{3+}, and approximate estimates of V\textsubscript{2}O\textsubscript{3}\textsuperscript{3+} concentrations in typical electrolytes.\textsuperscript{46}

In this paper, we report results for the UV-Vis spectroscopy of VFB catholytes over a range of concentrations and extend our model\textsuperscript{47} to analyze electrolytes with different concentrations of total vanadium. We characterize the data in terms of standard parameters that enable spectra to be simulated for any vanadium concentration and mixture ratio, providing a precise quantitative basis for measurement of SoC.

### Experimental

Stock solutions of V\textsuperscript{IV} were prepared from VOSO\textsubscript{4} and H\textsubscript{2}SO\textsubscript{4} (typically 2 mol dm\textsuperscript{–3} V\textsuperscript{IV} and 4 mol dm\textsuperscript{–3} sulfate). Stock solutions of V\textsuperscript{V} were prepared by electrochemical oxidation of the V\textsuperscript{IV} solution in a flow cell. End-points were determined by monitoring the potential of a carbon probe electrode and verified by color changes in the electrolyte. These solutions were then used to prepare series of other concentrations of V\textsuperscript{IV}, V\textsuperscript{V} and V\textsuperscript{IV}-V\textsuperscript{V} mixtures. Because samples were relatively small ($\sim$10 cm$^3$), volumes were measured by weighing and converting to volume by accurately measured densities. This precise method of mixing calibrated samples gave precise values of mole fraction and concentration. The total concentration of sulfate was 4 mol dm$^{-3}$ in all solutions.

Vanadium concentrations were determined against standard 0.1 M K\textsubscript{2}MnO\textsubscript{4} (Fisher Scientific) and H\textsubscript{2}SO\textsubscript{4} concentrations were determined against standard 0.1 M KOH (Sigma-Aldrich). VOSO\textsubscript{4} (vanadyl (IV) sulfate hydrate 97%) and H\textsubscript{2}SO\textsubscript{4} (sulfuric acid 98%) were obtained from Sigma-Aldrich. Water was distilled and deionized to a resistivity of $\sim$18 M$\Omega$ cm.

All spectroscopic measurements were made (ex-situ) with a commercial UV-Vis spectrophotometer ( Cary 4000 or Cary 5000, Varian) using quartz cells with a path length of 1 mm (Starna Scientific) for concentrations $<1$ mol dm$^{-3}$ or 0.2 mm (Hellma Analytics) for concentrations $>$1 mol dm$^{-3}$. The reference sample was 4 mol dm$^{-3}$ H\textsubscript{2}SO\textsubscript{4}. The scan rate was 10 nm s$^{-1}$ and the wavelength range was 200–900 nm. Absorbance measurements were recorded at wavelength intervals of 1 nm.

### Results and Discussion

**Spectra of electrolytes at various concentrations.** — At each of six different concentrations of total vanadium, solutions of V\textsuperscript{IV}, V\textsuperscript{V} and a series of mixtures were prepared as shown in Table I (Solution Set A). The UV-Vis spectrum of each solution is shown in Fig. I. For example, Fig. 1a shows the measured spectra for a vanadium concentration of 1.600 mol dm$^{-3}$. In agreement with earlier results,\textsuperscript{47} it is observed that the absorbance varies with percentage of V\textsuperscript{IV} in a very non-linear manner. Thus, for example, at wavelengths greater than 600 nm where the V\textsuperscript{V} parent solution has negligible absorbance, the 50% V\textsuperscript{IV} solution is more absorbing than the 72% solution, which in turn is more absorbing than the 88% solution and the 100% solution. In fact, the absorbance of the 50% solution at 760 nm (i.e. the V\textsuperscript{IV} absorbance peak) exceeds that of the 100% solution (i.e. the parent V\textsuperscript{V} solution) by a factor of almost 2 (rather than the expected factor of 0.5). This excess absorbance will be discussed in detail later.

At each concentration, i.e. within each of Figs. 1a to 1f, the trend as the mole percentage changes from 0% to 100% is broadly similar. Also, the absorbance decreases as concentration decreases for any given mole percentage as expected (Figs. 1a to 1f). However, it generally decreases faster for the mixtures than for the V\textsuperscript{IV} parent solution (100%). For example, at 760 nm the absorbance at 50% decreases steadily from Fig. 1a to 1f, eventually becoming less than the absorbance of the 100% solution.

**Determination of SoC.** — In a typical VFB, the catholyte consists of V\textsuperscript{IV} and V\textsuperscript{V} in H\textsubscript{2}SO\textsubscript{4}. All of the vanadium in a fully discharged catholyte is in the form of V\textsuperscript{IV} and during charging this is converted to V\textsuperscript{V}. Thus the mole percentage of V\textsuperscript{V} represents the SoC of the catholyte.

It is clear from Fig. 1 that, unlike the anolyte, where absorbance varies linearly with mixture ratio,\textsuperscript{6,47,53,55–57,72} it is not straightforward to determine the SoC of the catholyte. We can attempt to use a calibration curve such as that shown in Fig. 2, where measured absorbance at 760 nm is plotted against mole percentage of V\textsuperscript{V}. However, in the example shown in Fig. 2 it is clear that, for absorbance greater than $\sim$16 cm$^{-1}$, SoC is not uniquely determined by an absorbance measurement at 760 nm. For example, an absorbance measurement of $\sim$20.5 cm$^{-1}$ for an electrolyte sample can correspond to a SoC of either $\sim$20% or $\sim$50%. This problem can be overcome by using absorbance measurements at two different wavelengths. Thus, Fig. 2 also shows a plot of measured absorbance against SoC at 520 nm. An absorbance measurement of the same electrolyte sample at 520 nm

<table>
<thead>
<tr>
<th>Mole percentage of V\textsuperscript{IV}</th>
<th>Nominal</th>
<th>Actual</th>
<th>Total vanadium concentration C (mol dm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.3481</td>
<td>0.5992</td>
</tr>
<tr>
<td>5</td>
<td>5027</td>
<td>0.3475</td>
<td>0.5956</td>
</tr>
<tr>
<td>18</td>
<td>17.99</td>
<td>0.3488</td>
<td>0.5964</td>
</tr>
<tr>
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<td>50.08</td>
<td>0.3503</td>
<td>0.5999</td>
</tr>
<tr>
<td>72</td>
<td>71.86</td>
<td>0.3596</td>
<td>0.6014</td>
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<td>100</td>
<td>0.3481</td>
<td>0.5958</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td>0.3503</td>
<td>0.5978</td>
<td>0.8500</td>
</tr>
<tr>
<td><strong>Standard Deviation</strong></td>
<td>0.0042</td>
<td>0.0023</td>
<td>0.0030</td>
</tr>
</tbody>
</table>
Figure 1. Measured absorbance spectra of the $\text{V}^{\text{IV}}$-$\text{V}^{\text{IV}}$ mixtures in Solution Set A. Each of (a)–(f) corresponds to a column in Table I. The nominal mole percentages of $\text{V}^{\text{IV}}$ are shown; the $\text{V}^{\text{IV}}$ and $\text{V}^{\text{IV}}$ parent solutions are indicated as 100% and 0% respectively. The absorbance is expressed per unit length (cm$^{-1}$); the actual path length of the cell was 0.2 mm for (a), (b) and (c) and 1 mm for (d), (e) and (f). We note that the absorbance scales are not the same for all plots.

Spectra were obtained with a Cary 4000 spectrophotometer.

will also correspond to two possible values of SoC. However, only one of these values (the true SoC) will be equal to one of the corresponding two values at 760 nm. For example, if the true value of SoC is 20%, then an absorbance of 7.7 cm$^{-1}$ is obtained at 520 nm as shown in Fig. 2. If the true value of SoC were 50% then an absorbance of 11.7 cm$^{-1}$ would be obtained at 520 nm.

Thus, it is possible in principle to determine the SoC of catholytes from absorbance measurements. However, the procedure involves measurements (and corresponding calibration curves) at two different wavelengths. In practice, both calibration curves will vary with electrolyte composition not only in the values of absorbance but also in the shape of the curves. The variation of absorbance with total vanadium concentration is apparent in Fig. 1 and we have also observed a strong variation with sulfate concentration. Thus, in the case of the catholyte, a good quantitative understanding of the behavior of absorbance with electrolyte composition needs to be obtained before...
The concept of excess absorbance is key to such an understanding.

Excess absorbance.— The excess absorbance $A_{ex}$ is defined as the difference between the measured absorbance $A_m$ and the expected absorbance $A_{LC}$ calculated from a linear combination of the two components, $V^{IV}$ and $V^{V}$, in the mixtures. Thus,

$$A_{ex} = A_m - A_{LC}$$  \[1\]

where

$$A_{LC} = f A_4 + (1-f) A_5,$$  \[2\]

$f$ is the mole fraction of $V^{IV}$, and $A_4$ and $A_5$ are the measured absorbance values of the $V^{IV}$ and $V^{V}$ parent solutions, respectively.

Fig. 3 shows plots of measured, expected, and excess absorbance, $A_m$, $A_{LC}$, and $A_{ex}$ respectively, for a typical mixture (50% $V^{IV}$ and 50% $V^{V}$). Values of $A_m$ were calculated by Eq. 1 and values of $A_{LC}$ were calculated by Eq. 2. It can be seen that the excess absorbance $A_{ex}$ is the dominant component of the measured absorbance $A_m$, exceeding the expected absorbance $A_{LC}$ at all wavelengths. Thus, even at 760 nm (an absorbance peak for $V^{IV}$), the excess absorbance $A_{ex}$ exceeds the absorbance of the $V^{IV}$ in the mixture.

Values of $A_{ex}$ were similarly estimated for each of the mixtures at each of the concentrations in Fig. 1 and are plotted in Fig. 4. Clearly, there is significant excess absorbance over most of the wavelength range for each mixture at each concentration. It can be seen that each spectrum has a similar shape, with peaks at ~823 nm, ~670 nm and ~570 nm, separated by shallow troughs. Below 570 nm the absorbance decreases significantly. At all wavelengths, the excess absorbance is greatest for the 50% mixture; it decreases continuously as the mole percentage increases above, or decreases below 50%.

We have proposed that the excess absorbance behavior of the electrolyte is due to formation of a 1:1 complex between $V^{IV}$ and $V^{V}$. This may be represented by the equilibrium

$$V^{IV} + V^{V} \rightleftharpoons V_2O_3^{3+}.$$  \[3\]

where $V_2O_3^{3+}$ is a mixed-valence complex of $V^{IV}$ and $V^{V}$. The equilibrium constant $K_c$ for Eq. 3 may be written as

$$K_c = \frac{[V_2O_3^{3+}]}{[V^{IV}][V^{V}]}$$  \[4\]

where square brackets represent concentration.

For a mixed solution of $V^{IV}$ and $V^{V}$ with a total vanadium concentration $C$ and a mole fraction $f$ of $V^{IV}$, Eq. 4 gives

$$[V_2O_3^{3+}] = \frac{1 - \sqrt{1 - 4\chi^2 f(1-f)C^2}}{2\chi}$$  \[5\]

which approximates to

$$[V_2O_3^{3+}] \approx \chi C f(1-f)$$  \[6\]

when $K_C C < 0.4$. Therefore

$$\chi \approx \frac{[V_2O_3^{3+}]}{C^2 f(1-f)}$$

Thus $\chi$ approximates to a concentration quotient expressed in terms of $[V_2O_3^{3+}]$ and the total (complexed and uncomplexed) concentrations of $V^{IV}$ and $V^{V}$. We call $\chi$ the nominal equilibrium constant.

The measured absorbance $A_m$ is the sum of the absorbances due to VO$^{2+}$, VO$^{3+}$ and $V_2O_3^{3+}$ respectively:

$$A_m = \varepsilon_4 [VO^{2+}] + \varepsilon_5 [VO^{3+}] + \varepsilon_{45} [V_2O_3^{3+}].$$  \[7\]

where $\varepsilon_4$, $\varepsilon_5$, and $\varepsilon_{45}$ are the molar extinction coefficients of VO$^{2+}$, VO$^{3+}$ and $V_2O_3^{3+}$ respectively at a given wavelength.

The absorbances of the parent solutions, $A_4$ and $A_5$ in Eq. 2, can be written as

$$A_4 = \varepsilon_4 C$$

$$A_5 = \varepsilon_5 C$$  \[8\]

$^a$ All absorbances are per unit path length.

$^b$ Approximating the square-root term in Eq. 7 to $1 - 2\chi f(1-f)C^2$ is accurate within 1% when $K_C C < 1$. However $[V_2O_3^{3+}]$ is accurate within 1% only when $K_C C < 0.4$ because the numerator is rather small compared to 1.
and so Eq. 1 gives

$$A_{ex} = A_m - \varepsilon_4 f C - \varepsilon_5 (1 - f) C.$$  \[11\]

We note that $\varepsilon_4 f C$ and $\varepsilon_5 (1 - f) C$ are the values of absorbance that $V^{IV}$ and $V^V$ would have if they were present entirely as VO$^{2+}$ and VO$^{2+}$, respectively, in the mixtures (i.e. in the absence of V$_2$O$_3^{3+}$ formation). Substituting for $A_m$ from Eq. 9 we obtain

$$A_{ex} = \varepsilon_4 [\text{VO}^{2+}] + \varepsilon_5 [\text{VO}^{2+}] + \varepsilon_4 f C - \varepsilon_5 (1 - f) C.$$  

and substituting for [VO$^{2+}$] and [VO$^{2+}$] gives

$$A_{ex} = \varepsilon_{ex} [\text{V}_2\text{O}_3^{3+}],$$  \[12\]

where

$$\varepsilon_{ex} = \varepsilon_4 f - \varepsilon_4 - \varepsilon_5.$$  \[13\]

We call $\varepsilon_{ex}$ the excess molar extinction coefficient; it has a term ($\varepsilon_{45}$) for the absorbance due to V$_2$O$_3^{3+}$ and terms ($\varepsilon_4$ and $\varepsilon_5$) for the
decrease in absorbance due to lowering of $[\text{VO}^{2+}]$ and $[\text{VO}_2^{2+}]$ by formation of $\text{V}_2\text{O}_5^{3+}$. Substituting for $[\text{V}_2\text{O}_5^{3+}]$ in Eq. 12 from Eq. 8 we obtain

$$A_{ex} \approx \varepsilon_{ex} \chi C^2 f(1 - f) \quad [14]$$

$$= \varepsilon_{ex} \chi C^2 (f - f^2). \quad [15]$$

Substituting Eqs. 14 and 2 in Eq. 1 gives

$$A_m \approx f A_4 + (1 - f) A_5 + \varepsilon_{ex} \chi f(1 - f) C^2. \quad [16]$$

Substituting Eqs. 10 in Eq. 16 gives

$$A_m \approx f \varepsilon_4 C + (1 - f) \varepsilon_5 C + \varepsilon_{ex} \chi f(1 - f) C^2 \quad [17]$$

$$= \varepsilon_5 C + (\varepsilon_{ex} \chi C^2 + \varepsilon_4 C - \varepsilon_5 C) f - \varepsilon_{ex} \chi C^2 f^2. \quad [18]$$

**Variation of measured and excess absorbance with mole fraction of $\text{V}^{IV}$.**—Since $\varepsilon_{ex}$, $\varepsilon_5$ and $\varepsilon_{ex}$ are constant at any given wavelength, if $\chi$ and $C$ are also constant, then Eqs. 15 and 18 are second-order polynomial equations in $f$. Eq. 18 has zero-, first-, and second-order coefficients

$$\alpha_0 = \varepsilon_5 C, \quad [19]$$

$$\alpha_1 = \varepsilon_{ex} \chi C^2 + \varepsilon_4 C - \varepsilon_5 C \quad [20]$$

and

$$\alpha_2 = -\varepsilon_{ex} \chi C^2, \quad [21]$$

respectively. Eq. 15 has zero-order coefficient

$$\beta_0 = 0,$$

equal but opposite first and second-order coefficients

$$\beta_1 = -\beta_2 = \varepsilon_{ex} \chi C^2 \quad [22]$$

and a maximum at $f = 0.5$. If $K_e$ and $C$ are both constant, then $\chi$ is also constant from Eq. 6.

Thus, plots against mole fraction should give good fits to second order polynomials for both measured absorbance $A_m$ and excess absorbance $A_{ex}$. Such plots are shown in Figs. 5a and 5b, for a vanadium concentration of 0.850 mol dm$^{-3}$, at several representative wavelengths. These plots show excellent fits to second-order polynomials; the zero-, first- and second-order coefficients and the coefficients of determination $R^2$ are shown in Table II.

Revisiting Eq. 14, a plot of excess absorbance $A_{ex}$ against $f(1 - f)$ should give a straight line through the origin with a slope

$$m = \varepsilon_{ex} \chi C^2. \quad [23]$$

Such a plot is shown in Fig. 5c for the excess absorbance data from Fig. 5b. In all cases, a good fit to a straight line is obtained; the slopes, intercepts and coefficients of determination $R^2$ are shown in Table II.

Similar results were obtained for the other vanadium concentrations investigated. At all concentrations, plots of both measured absorbance and excess absorbance versus $f$ at any given wavelength gave good fits to second-order polynomials; examples at 760 nm are shown in Fig. 6a and Fig. 6b. Likewise plots of excess absorbance versus $f(1 - f)$ at any given wavelength gave good fits to straight lines; examples of such plots at 760 nm are shown in Fig. 6c.

**The excess absorbance parameter $p$.**—The excess molar extinction coefficient $\varepsilon_{ex}$ defined by Eq. 13, is a measure of the excess absorbance per unit concentration of $\text{V}_2\text{O}_5^{3+}$. In principle we can estimate $\varepsilon_{ex}$ at any wavelength from Eq. 14 if we know the value of the nominal equilibrium constant $\chi$ but this is difficult to determine accurately. Thus we therefore define an excess absorbance parameter

$$p = \varepsilon_{ex} \chi \quad [24]$$

for use as an alternative to $\varepsilon_{ex}$ when accurate values of $\chi$ are not available. At any wavelength $\lambda$, the parameter $p$ is directly proportional to $\varepsilon_{ex}$ (when $K_e$ and $C$ are both constant). Consequently, a plot of $p$ versus $\lambda$ is effectively equivalent to a plot of $\varepsilon_{ex}$ versus $\lambda$. Substituting Eq. 24 in Eq. 17 gives

$$A_m \approx \varepsilon_5 f C + \varepsilon_{ex} (1 - f) C + pf(1 - f) C^2. \quad [25]$$

From Eq. 14

$$p = \frac{A_{ex}}{f(1 - f) C^2} = \frac{A_{ex}}{[\text{VIV}][\text{VV}]} \quad [26]$$

Figure 5. Typical plots of (a) measured absorbance $A_m$ and (b) excess absorbance $A_{ex}$ versus mole fraction $f$ of $\text{V}^{IV}$ at four different wavelengths; (c) corresponding plots of excess absorbance $A_{ex}$ versus $f(1 - f)$. The lines represent least-squares best fits to second-order polynomials in (a) and (b), and to straight lines in (c). The coefficients are shown in Table II. The total vanadium concentration was 0.850 mol dm$^{-3}$. 
From plots of \( A \) versus \( f \) From plots of \( f \) and \( f \) From Eq. 26 we see that \( p \) is referenced to the concentrations \([\text{V}^{\text{IV}}]\) rather than to \([\text{V}_2\text{O}_3^{3+}]\), to which \( \varepsilon_{\text{ex}} \) is referenced and which is difficult to determine accurately.

Thus, we can evaluate \( p \) at each wavelength even though we cannot easily evaluate \( \varepsilon_{\text{ex}} \). We can do this by three different methods:

(i) From plots of \( A_{\text{m}} \) or \( A_{\text{ex}} \) versus \( f \). Determine a second-order polynomial least-squares best fit to a plot of \( A_{\text{m}} \) versus \( f \) such as in Fig. 5a and from the first- and second-order coefficients obtain values of \( p \):

\[
p_{\alpha 1} = \frac{\alpha_1 - A_4 + A_5}{C^2}
\]

and

\[
p_{\alpha 2} = \frac{-\alpha_2}{C^2}
\]

using Eqs. 10, 20, 21 and 24. Alternatively, determine a second-order polynomial least-squares best fit to a plot of \( A_{\text{ex}} \) versus \( f \) such as in Fig. 5b and from the first- and second-order coefficients obtain values of \( p \):

\[
p_{\beta 1} = \frac{\beta_1}{C^2}
\]

and

\[
p_{\beta 2} = \frac{-\beta_2}{C^2}
\]

using Eqs. 22 and 24.

The second-order coefficients of both polynomials are exactly equal and

\[
\beta_1 = \alpha_1 - A_4 + A_5
\]

from Eqs. 10, 20, 21 and 22. Therefore

\[
p_{\alpha 1} = p_{\beta 1} = p_1
\]

and

\[
p_{\alpha 2} = p_{\beta 2} = p_2.
\]

(ii) From plots of \( A_{\text{ex}} \) versus \( f(1 - f) \). Determine a linear least-squares best-fit line to a plot of \( A_{\text{ex}} \) versus \( f(1 - f) \) such as in Fig. 5c. From the slope of each of these lines obtain a value of \( p \)

\[
p = \frac{m}{C^2}
\]

using Eqs. 23 and 24.

From Eq. 26 we see that \( p \) is referenced to the concentrations \([\text{V}^{\text{IV}}]\) and \([\text{V}^{\text{IV}}]\) rather than to \([\text{V}_2\text{O}_3^{3+}]\), to which \( \varepsilon_{\text{ex}} \) is referenced and which is difficult to determine accurately.

Thus, we can evaluate \( p \) at each wavelength even though we cannot easily evaluate \( \varepsilon_{\text{ex}} \). We can do this by three different methods:

(i) From plots of \( A_{\text{m}} \) or \( A_{\text{ex}} \) versus \( f \). Determine a second-order polynomial least-squares best fit to a plot of \( A_{\text{m}} \) versus \( f \) such as in Fig. 5a and from the first- and second-order coefficients obtain values of \( p \):

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p_{\alpha 1} = \frac{\alpha_1 - A_4 + A_5}{C^2}
\]

and

\[
p_{\alpha 2} = \frac{-\alpha_2}{C^2}
\]

using Eqs. 10, 20, 21 and 24. Alternatively, determine a second-order polynomial least-squares best fit to a plot of \( A_{\text{ex}} \) versus \( f \) such as in Fig. 5b and from the first- and second-order coefficients obtain values of \( p \):

\[
p_{\beta 1} = \frac{\beta_1}{C^2}
\]

and

\[
p_{\beta 2} = \frac{-\beta_2}{C^2}
\]

using Eqs. 22 and 24.

The second-order coefficients of both polynomials are exactly equal and

\[
\beta_1 = \alpha_1 - A_4 + A_5
\]

from Eqs. 10, 20, 21 and 22. Therefore

\[
p_{\alpha 1} = p_{\beta 1} = p_1
\]

and

\[
p_{\alpha 2} = p_{\beta 2} = p_2.
\]

(ii) From plots of \( A_{\text{ex}} \) versus \( f(1 - f) \). Determine a linear least-squares best-fit line to a plot of \( A_{\text{ex}} \) versus \( f(1 - f) \) such as in Fig. 5c. From the slope of each of these lines obtain a value of \( p \)

\[
p = \frac{m}{C^2}
\]

using Eqs. 23 and 24.

(iii) From \( A_{\text{ex}} \) and \( f \). Estimate a value of \( p \) (call it \( p_1 \)) at each mole fraction \( f \) directly from the measured values of \( A_{\text{ex}} \) using Eq. 26. Then estimate the average \( p \) at each wavelength.

In the case of Method (i), we can also extract values of \( \varepsilon_4 \) and \( \varepsilon_5 \) from the coefficients of the polynomial fit of \( A_{\text{m}} \) versus \( f \) since, from Eqs. 19, 20 and 21,

\[
\varepsilon_4 = \frac{\alpha_0 + \alpha_1 + \alpha_2}{C} \quad \text{and} \quad \varepsilon_5 = \frac{\alpha_0}{C}.
\]
Table III. Values of \( p_1, p_2, \) and \( p_3 \) determined from the plots in Fig. 5 using Methods (i) and (ii) and corresponding values of \( \bar{p} \) obtained by Method (iii). The average values \( \bar{p} \) and standard deviations \( \sigma \) are also shown.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>520 nm</th>
<th>580 nm</th>
<th>660 nm</th>
<th>760 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p_1 )</td>
<td>( \rho_{u1} = \rho_{f1} )</td>
<td>61.11</td>
<td>83.19</td>
<td>79.16</td>
<td>68.63</td>
</tr>
<tr>
<td>( p_2 )</td>
<td>( \rho_{u2} = \rho_{f2} )</td>
<td>61.54</td>
<td>83.90</td>
<td>78.85</td>
<td>69.29</td>
</tr>
<tr>
<td>( p_3 )</td>
<td>( mc^2 )</td>
<td>61.41</td>
<td>84.29</td>
<td>80.39</td>
<td>70.02</td>
</tr>
<tr>
<td>( \bar{p} )</td>
<td>Average over ( f ) of ( \rho = \rho_{ex}/[f(1-f)c^2] )</td>
<td>61.15</td>
<td>83.29</td>
<td>79.26</td>
<td>68.74</td>
</tr>
<tr>
<td>( \bar{f} )</td>
<td>( (p_1 + p_2 + p_3)/4 )</td>
<td>61.30</td>
<td>83.66</td>
<td>79.66</td>
<td>69.17</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>Standard deviation of ( p )</td>
<td>0.21</td>
<td>0.52</td>
<td>0.57</td>
<td>0.63</td>
</tr>
</tbody>
</table>

![Figure 7](image-url)  
**Figure 7.** (a) Values of \( p_1, p_2, p_3, \) and \( \bar{p} \) estimated by Methods (i)–(iii) as described in the text for a vanadium concentration of 0.850 mol dm\(^{-3}\). The standard deviation \( \sigma \) from the mean \( \bar{p} \) is also plotted. (b) Values of \( \varepsilon_4 \) and \( \varepsilon_5 \) obtained from plots of \( A_{ex}/C^2 \) versus \( f \) using Eq. 10 (dashed lines) and from the absorbances \( A_1 \) and \( A_2 \) of the 0.850 mol dm\(^{-3}\) parent VIV and V\(^{3+}\) solutions using Eqs. 10 (solid lines).

These can then be compared with the corresponding values obtained from \( A_1 \) and \( A_2 \) by Eqs. 10, as a check on the robustness of the analysis.

Values of \( p_1, p_2, \) and \( p_3 \) determined from the plots in Fig. 5 using Methods (i) and (ii) are shown in Table III. Corresponding values of \( \bar{p} \) obtained by Method (iii) are also shown. It can be seen that they are in excellent agreement.

Values of \( p_1, p_2, p_3, \) and \( \bar{p} \) determined in this way at each wavelength in the range 550–900 nm are plotted\(^a\) in Fig. 7a for a vanadium concentration of 0.850 mol dm\(^{-3}\). It can be seen that there is good agreement between the values of \( p \) obtained by the different methods: the standard deviation \( \sigma \) from the mean \( \bar{p} \) is also plotted. The values of \( \varepsilon_4 \) and \( \varepsilon_5 \) obtained using Eqs. 32 are compared in Fig. 7b with the corresponding values obtained directly from the absorbances \( A_1 \) and \( A_2 \) of the VIV and V\(^{3+}\) parent solutions. It can be seen that there is reasonable agreement.

Variation of \( p \) with vanadium concentration.—From Eq. 26, a plot of \( A_{ex}/C^2 \) versus \( f(1-f) \) has a slope of \( p \) and so, at any given wavelength, such a plot at any value of \( C \) should fall on the same straight line if \( p \) were independent of \( C \). The data in Fig. 6c is replotted in Fig. 8 in the form of \( A_{ex}/C^2 \) versus \( f(1-f) \). It is clear from Fig. 8 that, although the plot at each value of \( C \) shows good linearity, the slope varies somewhat with \( C \). This is expected since, from Eqs. 6 and 24, \( p \) is expected to vary with \( C \).

Using Methods (i)–(iii) from the previous section, we determined values of \( p \) at each concentration investigated. Mean values \( \bar{p} \) and standard deviations are shown in Table IV for selected wavelengths; \( \bar{p} \) is plotted against wavelength in Fig. 9. We see that the spectra of \( p \) have a similar shape at all concentrations, and exhibit peaks at \( \sim 572 \) nm, \( \sim 666 \) nm and \( \sim 823 \) nm. The \( p \) values are observed to decrease as concentration increases. Thus, although \( p \) has a unique value at each wavelength at any given concentration, the value varies with concentration. It follows that, although a single plot of \( p \) versus \( \lambda \) at a given vanadium concentration is sufficient to enable the reconstruction of the excess absorbance spectrum (and therefore the measured absorbance spectrum) of any VIV-V\(^{3+}\) mixture at that concentration, if we want to do this at any concentration we need a parameter that quantitatively expresses the variation of \( p \) with concentration.

Values of \( p \) obtained from Fig. 9 are plotted in Fig. 10 against vanadium concentration \( C \) for four selected wavelengths. It can be seen that \( p \) shows a relatively small variation with \( C \). To fully express this variation would require a separate plot at each wavelength of interest. However, the variation of \( p \) with \( C \) reflects the variation of \( \chi \) with \( C \) and so is independent of wavelength. Indeed we note from

\(^a\)We note here an error in an earlier paper: in Fig. 11 of Ref. 47, the scale on the \( p \)-axis is incorrect.

![Figure 8](image-url)  
**Figure 8.** Plot of \( A_{ex}/C^2 \) versus \( f(1-f) \) for the data in Fig. 6.
Table IV. Mean values $\bar{\rho}$ and standard deviations $\sigma$ obtained from averaging $p_1$, $p_2$, $p_1$, and $p_2$ for each concentration at 572 nm, 666 nm, 760 nm, and 823 nm. Values of $p_1$ and $p_2$ were determined by Method (i), $p_1$ by Method (ii) and $p_2$ by Method (iii) as described in the text.

<table>
<thead>
<tr>
<th>Concentration (mol dm$^{-3}$)</th>
<th>572 nm</th>
<th>666 nm</th>
<th>760 nm</th>
<th>823 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\bar{\rho} \pm \sigma$</td>
<td>$\bar{\rho} \pm \sigma$</td>
<td>$\bar{\rho} \pm \sigma$</td>
<td>$\bar{\rho} \pm \sigma$</td>
</tr>
<tr>
<td>0.350</td>
<td>93.48 ± 1.07</td>
<td>88.74 ± 1.18</td>
<td>77.49 ± 1.15</td>
<td>81.39 ± 1.03</td>
</tr>
<tr>
<td>0.598</td>
<td>89.74 ± 0.38</td>
<td>84.79 ± 0.33</td>
<td>73.46 ± 0.32</td>
<td>77.61 ± 0.36</td>
</tr>
<tr>
<td>0.850</td>
<td>84.15 ± 0.50</td>
<td>79.80 ± 0.58</td>
<td>69.17 ± 0.63</td>
<td>73.17 ± 0.72</td>
</tr>
<tr>
<td>1.102</td>
<td>80.75 ± 2.96</td>
<td>75.87 ± 3.35</td>
<td>68.43 ± 3.43</td>
<td>72.38 ± 3.74</td>
</tr>
<tr>
<td>1.347</td>
<td>78.17 ± 1.40</td>
<td>73.33 ± 1.54</td>
<td>64.43 ± 1.58</td>
<td>68.27 ± 1.72</td>
</tr>
<tr>
<td>1.600</td>
<td>75.53 ± 0.74</td>
<td>72.04 ± 0.87</td>
<td>62.60 ± 0.93</td>
<td>66.39 ± 1.03</td>
</tr>
</tbody>
</table>

Figure 10. Plot of $\rho$ versus vanadium concentration $C$ at selected wavelengths. Values of $\rho$ are from the data in Fig. 9. The selected wavelengths correspond to the peaks in Fig. 9 and the $\text{V}^{2+}$ absorbance peak (760 nm).

Figure 11. Plots of $\phi_r$ versus wavelength for six values of concentration as indicated. The reference concentration is $C_r = 0.850$ mol dm$^{-3}$ and so $\phi_r$ is written as $\phi_{r,0.85}$. Values were calculated at each wavelength at each concentration from the values of $\rho$ in Fig. 9, using Eq. 34.

Indeed observed for each of the plots in Fig. 10. However, $K_c$ may also vary with $C$ and this may cause further variation in $p$, in addition to the direct dependence of $p$ on $C$. Increasing $K_c$ in Eq. 33 causes an increase in $p$. Thus, the results in Fig. 10 indicate that if $K_c$ increases with increasing $C$ its effect is not sufficiently large to overcome the direct dependence of $p$ on $C$ in Eq. 33. If, on the other hand, $K_c$ decreases with increasing $C$ the effect will be to cause $p$ to decrease more rapidly with increasing $C$.

In order to quantify the variation of $p$ with $C$, we choose a reference concentration $C_r$ and define a parameter

$$\phi_r = \frac{p(\lambda, C)}{p(\lambda, C_r)}$$

that relates the value of $p(\lambda, C)$ at any given concentration $C$ and wavelength $\lambda$, to the corresponding value $p(\lambda, C_r)$ at $C_r$. Substituting Eq. 24 in Eq. 34

$$\phi_r = \frac{\varepsilon_k(\lambda)\chi(C)}{\varepsilon_k(\lambda)\chi(C_r)} = \frac{\chi(C)}{\chi(C_r)}$$

Thus, although $\phi_r$ can be estimated by Eq. 34 at any wavelength, Eq. 35 shows that it should have similar values at all wavelengths at any given concentration $C$. Therefore we can regard $\phi_r$ as a function of $C$ only and evaluate it at any given $C$ by taking the average over a range of wavelengths. We call $\phi_r$ the concentration coefficient of $p$ referenced to a concentration $C_r$.

Fig. 11 shows values of $\phi_r$ calculated from the values of $p$ in Fig. 9 for a reference concentration of 0.850 mol dm$^{-3}$ plotted against $\lambda$. We observe that $\phi_r$ is relatively constant at any given $C$. (At $C = C_r$, $K_c$ is the equilibrium constant expressed in terms of concentration and so may vary with the activity coefficients of the species in Eq. 4. The true constant is the equilibrium constant expressed in terms of thermodynamic activity.\(^4\))
The value of $\phi_r$ at each value of $C$ was obtained by averaging the values in Fig. 11 over all wavelengths in the range 550–900 nm. The reference concentration is 0.850 mol dm$^{-3}$ and so $\phi_r$ is written as $\phi_{0.85}$.

By definition $\phi_r = 1$. Values of $\phi_r$ estimated from the data in Fig. 11 by taking the average over the wavelength range 550 nm–900 nm are plotted against $C$ in Fig. 12. By interpolating between experimental values on this plot, we can read a value of $\phi_r$ at any concentration $C$ and use it in conjunction with the plot in Fig. 9 of $p$ versus $\lambda$ at the reference concentration $C_r = 0.850$ mol dm$^{-3}$ to generate a plot of $p$ versus $\lambda$ at $C$ since from Eq. [34]

$$p(\lambda, C) = \phi_r(C)p_r(\lambda),$$

where $p_r$ represents the values of $p$ at $C_r$.

Referencing $p$ and $\phi_r$ to the average vanadium concentration.— The precision of the values of $p(\lambda, C)$ obtained using Eq. [36] depends on the precision of $\phi_r(C)$ and $p_r(\lambda)$ and this is systematically sensitive to any error in the set of experiments at $C = C_r$. Error in that set of experiments will determine the precision of $p_r$ and furthermore it will influence the precision of $\phi_r$ much more than will error in experiments at other values of $C$. To avoid such a strong influence by any one set of experiments, we estimated values of $\phi_r$ using, as reference concentration $C_r$, each value of $C$ in turn. Such plots are shown in Fig. 13. At each $C$, the average of $\phi_r$ over the six reference concentrations $C_r$ was determined. These average values are plotted in Fig. 14. We show in Appendix A that they are equivalent to values of $\phi_r$ referenced to the average reference concentration $C_a$ and we therefore designate them as $\phi_a$.

In order to use $\phi_a$ to construct plots of $p(C)$ versus $\lambda$, we also need a reference plot of $p(C_a)$ versus $\lambda$. At a given $\lambda$, the average value of $1/p$ over a series of concentrations $C$ is

$$\frac{1}{p(C_a)} = \frac{1}{\varepsilon_a\chi(C_a)} = \frac{1}{\varepsilon_a\chi(C_a)} = \frac{1}{p(C_a)}$$

from Eq. [24] since

$$\frac{1}{\chi(C_a)} = \frac{1}{\chi(C_a)}$$

(see Appendix A, Eq. A2). The inverses of the values of $p$ in Fig. 9 were averaged over the six experimental concentrations at each wavelength. The inverses of these averages give values $p_a(\lambda) = p(C_a, \lambda)$ which are plotted against $\lambda$ in Fig. 15. This plot can be regarded as

Figure 12. Plot of $\phi_r$ versus $C$. The value of $\phi_r$ at each value of $C$ was obtained by averaging the values in Fig. 11 over all wavelengths in the range 550–900 nm. The reference concentration is 0.850 mol dm$^{-3}$ and so $\phi_r$ is written as $\phi_{0.85}$.

Figure 13. Plots of $\phi_r$ versus $C$ for six different reference concentrations as indicated. For each reference concentration $C_r$, a plot similar to Fig. 11 was generated and used to obtain a value of $\phi_r$ at each value of $C$ (as was done for $C_r = 0.850$ mol dm$^{-3}$ in Fig. 12).

Figure 14. Plot of $\phi_a$ versus $C$ (solid circles) where $\phi_a$ represents $\phi_r$ referenced to $C_a = 0.973$ mol dm$^{-3}$, the average of the reference concentrations in Fig. 13. At each value of $C$, the value of $\phi_a$ was obtained by averaging the values of $\phi_r$ in Fig. 13 over the six reference concentrations. As shown in Appendix A, this procedure gives values of $\phi_a$ as defined above. The line represents the values of $\phi_a$ obtained from Eq. 42 using a value of $M = 0.1930$ mol dm$^{-3}$ from Table V.

Figure 15. Plot of $p_a$ versus wavelength where $p_a(\lambda) = p(C_a, \lambda)$ and $C_a = 0.973$ mol dm$^{-3}$, the average of the set of concentrations in Fig. 9 (which is the same as the set of reference concentrations in Fig. 13). At each wavelength, the value of $p_a$ was determined as $p_a = 1/\chi(\lambda)$, where $\chi(\lambda)$ is the average of the inverses of the $p$-values in Fig. 9 over the six concentrations. From Eq. [37], this procedure gives values of $p_a$ as defined above.
Thus, if given \( C \), that there is good agreement between the values of the least-squares best-fit line are shown in Table V. It can be seen that Fig. 16a is linear within experimental error and in that case the value of \( M = (M_1 + M_2)/2 \).

### Table V. Coefficients of determination, slopes, and intercepts of the linear least-squares best-fit lines to the plot of \( \phi_a \) versus \( C \phi_a \), in Fig. 16a and the plot of 1/\( \phi_a \) versus \( C \) in Fig. 16b.

<table>
<thead>
<tr>
<th></th>
<th>Coefficient of determination ( R^2 )</th>
<th>Slope ((-M_1) (mol(^{-1}) dm(^3)))</th>
<th>Intercept (Q_1)</th>
<th>( Q_2 = 1 + M_1 C_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \phi_a ) versus ( C \phi_a )</td>
<td>0.9785</td>
<td>-0.1931</td>
<td>1.1880</td>
<td>1.1879</td>
</tr>
</tbody>
</table>
| 1/\( \phi_a \) versus \( C \)     | 0.9842                                  | 0.1625                                      | 0.8419            | 0.1930                   

**Fig. 16a:** Plot of \( \phi_a \) versus \( C \phi_a \)  
**Fig. 16b:** Plot of 1/\( \phi_a \) versus \( C \)

Thus, a plot is shown in Fig. 16a for the data from Fig. 14. Good linearity is obtained; the slope, intercept and coefficient of determination of the least-squares best-fit line are shown in Table V. We can obtain an alternative value of \( M \) from this plot since

\[
\phi_a (C) = 1 + MC_c - MC \phi_a (C)
\]  
and so

\[
\phi_a (C) = 1 + MC_c.
\]

Alternatively from Eq. 42

\[
\frac{1}{\phi_a (C)} = \frac{1}{1 + MC_c} + \frac{MC}{1 + MC_c}.
\]

From \( M \) we can obtain values of \( \phi_a (C) \) at any concentration \( C \) using Eq. 42. As shown in Table V, the average value of \( M \) obtained from the slopes of Figs. 16a and 16b is \( M = 0.1930 \) mol\(^{-1}\) dm\(^3\). A plot of \( \phi_a \) based on this value of \( M \) for \( C_c = 0.973 \) mol dm\(^{-3}\) is shown (as a line) in Fig. 14. It can be seen that there is excellent agreement with the values of \( \phi_a \) determined at the individual concentrations as described earlier.

Equation 42 is based on the empirical observation of the linearity of \( \phi_a \) versus \( C \phi_a \) and 1/\( \phi_a \) versus \( C \), which is demonstrated for \( C_c = C_a \) in Figs. 16a and 16b. However, we show in Appendix C that Eq. 42 is general and that \( M \) does not depend on reference concentration.

Although the plot in Fig. 16a is prompted by Eq. 40, the validity of Eq. 42 does not depend on \( K_c \) being constant. If \( K_c \) is constant then \( M = K_c \). However, it is possible for \( K_c \) to vary with \( C \) in such a way that Fig. 16a is linear within experimental error and in that case \( M \neq K_c \). Thus, the observed value of \( M = 0.1930 \) mol\(^{-1}\) dm\(^3\) can be regarded as a value of \( K_c \) only with the caveat that such an estimate of \( K_c \) is at best approximate.

### Standard spectra and governing equation for absorbance.

The reference spectrum of \( p \) in Fig. 15 and the corresponding plot of \( \phi_a \) versus \( C \) in Fig. 14 are both referenced to the average vanadium concentration \( C_a \). The value of \( C_a \) is determined by the particular set of spectroscopy experiments. We would prefer to use values of \( p \) and \( \phi_a \) referenced to a standard concentration \( C_0 \) so that different sets of measurements might be more easily compared.
by Eq. 48 using the standard spectra in Fig. 17 and the value£ of \( C_0 = 0.1930 \text{ mol} \cdot \text{dm}^{-3} \) from Table V. It can be seen that there is good agreement: the average error over the entire data set (42 spectra, each with \( \sim 350 \) different wavelengths for a total of \( \sim 14,700 \) points) is less than 3%. Thus, based on a single standard spectrum of \( p \) at a standard concentration, a single parameter \( M \) for concentration dependence and the measured extinction coefficients \( \varepsilon_4 \) and \( \varepsilon_5 \), we can reconstruct the spectrum of a \( \text{VIV}^\text{IV} - \text{VV} \) electrolyte over a wide range of concentrations and mixture ratios with reasonable accuracy.

Calibration curves for SoC, such as the examples shown in Fig. 2, will vary strongly with vanadium concentration. We can now quantify this variation and so generate a calibration curve for any concentration of vanadium. To do this we rewrite Eq. 48 in terms of the mole fraction, \( x = 1 - f \), of \( \text{VV} \); the percentage SoC is then \( S = 100x \). Substituting \( f = 1 - x \) in Eq. 48 we obtain

\[
A_m = a_0 + a_1 x + a_2 x^2
\]

where

\[
a_0 = C\varepsilon_4
\]

\[
a_1 = C(\varepsilon_5 - \varepsilon_4) + \frac{(1 + M C_0) p_0 C^2}{1 + MC}
\]

\[
a_2 = -\frac{(1 + M C_0) p_0 C^2}{1 + MC}
\]

Equation 49 expresses the variation of \( A_m \) with \( x \) at any given values of \( x \) and \( C \) and so it is the general equation for SoC calibration curves based on the governing equation, Eq. 48. The values of \( a_0, a_1 \) and \( a_2 \) depend on \( C \) and also on \( \lambda \), since \( \varepsilon_4, \varepsilon_5 \) and \( p_0 \) depend on \( \lambda \). Examples of calibration curves generated using Eq. 49 are compared in Fig. 19 with corresponding calibration points obtained from experimental data from Solution Set B. It can be seen that there is good agreement.

We can test the calibration curves in Fig. 19 by determining the SO of each of the mixtures at that concentration of vanadium (1.581 \text{ mol dm}^{-3}). At each wavelength, the SO is determined from the root of Eq. 49, i.e. candidate values of SO are \( S = 100x \) where

\[
x = -\frac{a_0 \pm \sqrt{a_0^2 - 4a_2(a_0 - A_m)}}{2a_2}
\]

Candidate values of SO determined in this way are shown in Table VI for the set of mixtures at \( C = 1.581 \text{ mol dm}^{-3} \). As described earlier, the true SO corresponds to the candidate value that coincides at the two wavelengths. It can be seen that there is good agreement between these values of SO and the corresponding values determined from the concentrations of the parent solutions. Values of SO determined from the absorbance spectra of the other mixtures in Set B similarly showed good agreement with the corresponding values determined from the concentrations of the parent solutions.

Thus, for any given total concentration of vanadium we can determine SO based on measurements at two wavelengths using the standard spectral data in Fig. 17 and the corresponding value of \( M \). In practice, the concentration of vanadium in the catholyte of a working VFB will usually not be known accurately. Even if it is initially known with good accuracy, it will change over time because of factors such as water and vanadium transfer across the membrane. However, we have shown\(^5\) that, based on measurements at three (or more) wavelengths, the total concentration of vanadium can be determined, in addition to the SO. Empirical methods based on comparing spectra from operating VFB catholytes to sets of experimental calibration spectra at different SOs cannot do this, even by utilizing measurements over a large spectral range.

1 The value of \( M \) depends on the sulfate concentration in the electrolyte. All electrolytes in this study had a sulfate concentration of 4 \text{ mol dm}^{-3}.  

---

**Figure 17.** Standard spectra generated from the measured spectra in Fig. 1. The values of \( p_0 \) are referenced to a standard concentration of vanadium, \( C_0 = 1 \text{ mol dm}^{-3} \). The spectrum of \( p_0 \) was obtained from the corresponding spectrum for \( C_0 = 0.973 \text{ mol dm}^{-3} \) in Fig. 15 using Eq. 46. The spectra of \( \varepsilon_4 \) and \( \varepsilon_5 \) are the averages of the values obtained from the spectra of the 0.350, 0.598, and 0.850 \text{ mol dm}^{-3} parent solutions of \( \text{VIV} \) and \( \text{VV} \) respectively, using 1 mm cells.

Replacing \( C_i \) with \( C_0 \) in Eq. 42 we obtain

\[
\phi_0 (C) = \frac{1 + MC_0}{1 + MC}.
\]

Similarly from Eqs. 38 and 42,

\[
p_0(\lambda) = p(C_0, \lambda) = \phi_0(C_0) p_0(\lambda) = \frac{1 + MC_0}{1 + MC} p_0(\lambda).
\]

Using Eq. 46 we can obtain a plot of \( p \) versus \( C \) referenced to a standard concentration \( C_0 \) from the corresponding plot referenced to the average experimental concentration \( C_i \). Such a plot is shown in Fig. 17 for a standard concentration \( C_0 = 1 \text{ mol dm}^{-3} \).

We rewrite Eq. 38 in terms of \( p_0 \) and \( \phi_0 \) referenced to the standard concentration \( C_0 \) as

\[
p(C, \lambda) = \phi_0(C) p_0(\lambda) = \frac{1 + MC_0}{1 + MC} p_0(\lambda).
\]

Equation 47 can be used in conjunction with the standard spectrum of \( p_0 \) in Fig. 17 to determine \( p \) at any wavelength at any concentration.

Substituting Eq. 47 in Eq. 25 we obtain

\[
A_m = \varepsilon_4 f C + \varepsilon_5 (1 - f) C + \frac{(1 + MC_0) p_0 (1 - f) C^2}{1 + MC}.
\]

Equation 48 is the governing equation summarizing our model of electrolyte absorbance. It expresses the absorbance \( A_m(\lambda) \) of an electrolyte with \( \text{VIV} \) mole fraction \( f \) and total vanadium concentration \( C \) in terms of \( \varepsilon_4(\lambda), \varepsilon_5(\lambda), p_0(\lambda) \) and \( M \). In order to use Eq. 48 to simulate spectra we need, in addition to \( p_0 \) and \( M \), spectra of \( \varepsilon_4 \) and \( \varepsilon_5 \). We determined these from the spectra of the parent \( \text{VIV} \) and \( \text{VV} \) solutions, respectively; the resulting values are plotted in Fig. 17.

In summary, the governing equation, Eq. 48, completely describes the absorbance behavior of a \( \text{VIV}^\text{IV} \)-\( \text{VV} \) electrolyte and can be used to simulate the spectrum for any \( \text{VIV}^\text{IV} - \text{VV} \) ratio and any concentration of vanadium. The necessary data for such a simulation are the standard spectra \( p_0, \varepsilon_4, \varepsilon_5 \) in Fig. 17 and the value of \( M \).

**Simulation of spectra and measurement of SoC.**—In order to independently compare simulations based on Eq. 48 with experiment, we prepared a separate set of catholyte solutions (Set B) with vanadium concentrations different from those of the solutions (Set A) used to generate the standard spectra and the value of \( M \). The experimentally measured spectra for the solutions in Set B, measured with a different spectrophotometer, are compared in Fig. 18 with spectra simulated...
Figure 18. Comparison between simulated (broken lines) and measured (solid lines) absorbance spectra of a range VIV-VV mixtures (Set B). The nominal mole percentages and average concentration are indicated in each case; precise values are listed in Appendix D. The simulated spectra were generated using Eq. 48 from the standard spectra in Fig. 17 and a value of \(M = 0.1930 \text{ mol}^{-1} \text{ dm}^3\) (from Table V), i.e. from a set of spectral parameters generated from an independent set of solutions, Set A. The spectra for Solution Set B were obtained with a Cary 5000 spectrophotometer, different from that (Cary 4000) used to obtain the spectra of Solution Set A.

Thus the model of spectral behavior developed in this paper (Eq. 48) and the associated standard spectral data (Fig. 17 and the value of \(M\)) provide a precise quantitative basis for measuring both the SoC and the total vanadium concentration of a VFB catholyte using a small number of wavelengths.

Conclusions

The ultraviolet-visible spectra of a range of VIV-VV sulfate electrolytes were measured and analyzed. Even though the spectra show a non-linear relationship with mole fraction of VV and with total vanadium concentration, it is shown that the state of charge of the electrolyte can be determined from calibration curves at two wavelengths.

Spectra of electrolytes with six different vanadium concentrations ranging from 0.350 to 1.600 mol dm\(^{-3}\) showed a similar variation with mole fraction \(f\) of VIV at each concentration. The variation was consistent with our model\(^{47}\) which assumes the formation of a mixed-valence V\(^{IV}\)-V\(^{V}\) complex \(\text{V}_2\text{O}_3\)\(^{3+}\) in equilibrium with \(\text{VO}^{2+}\) and \(\text{VO}_2^{+}\). Based on this model, the spectra were characterized in terms an excess absorbance parameter\(^{47}\) \(p\) and the molar extinction coefficients \(\varepsilon_4\) and \(\varepsilon_5\) of \(\text{VO}^{2+}\) and \(\text{VO}_2^{+}\), respectively.
Values of φ obtained by three different methods showed good agreement and plots against wavelength at each concentration showed that φ varies weakly with the vanadium concentration C in a similar manner at each wavelength. This variation was quantified by means of a concentration coefficient φC referenced to a concentration C1. It was shown theoretically that the average of the inverse of φ over a range of vanadium concentrations can be used to obtain its value (φ0) at the average concentration and, based on this, the spectrum of p was obtained for the average of the concentrations investigated. Similarly it was shown that the average of φ0 over a series of reference concentrations C1 is its value (φφ) referenced to their average, C2, based on this, a plot of φ0 versus C was obtained. Together, the plots of φ0 versus λ and φφ versus C contain all the data necessary to generate a spectrum of p at any concentration.

Values of φ obtained by three different methods showed good agreement and plots against wavelength at each concentration showed that φ varies weakly with the vanadium concentration C in a similar manner at each wavelength. This variation was quantified by means of a concentration coefficient φC referenced to a concentration C1. It was shown theoretically that the average of the inverse of φ over a range of vanadium concentrations can be used to obtain its value (φ0) at the average concentration and, based on this, the spectrum of p was obtained for the average of the concentrations investigated. Similarly it was shown that the average of φ0 over a series of reference concentrations C1 is its value (φφ) referenced to their average, C2, based on this, a plot of φ0 versus C was obtained. Together, the plots of φ0 versus λ and φφ versus C contain all the data necessary to generate a spectrum of p at any concentration.

It was shown theoretically for constant Kc that φ0 should vary linearly with C0φ0 and that 1/φφ should vary linearly with C. Our experimental data showed that plots of φ0 versus C0φ0 and plots of 1/φφ versus C are linear. Based on this linearity, Eq. 42 was derived which gives the value of φφ as a function of C as terms of its reference concentration and a single parameter M that is independent of reference concentration. A value of M = 0.1930 mol dm−1 was determined from the plots of φ0 versus C0φ0 and 1/φφ versus C.

A spectrum of p at a standard concentration C0 = 1 mol dm−1 was generated from the spectrum of p at the average vanadium concentration and the measured value of M. A governing equation

\[ A_m = e_4 f C + e_5 (1 - f) C + \frac{(1 + MC_C) p_0 f(1 - f) C^2}{1 + MC} \]  \[ [48] \]

was derived which expresses the absorbance, at any wavelength λ, of catholyte with any VIV mole fraction f and any total vanadium concentration C in terms of standard spectral parameters: the excess absorbance parameter p0, the molar extinction coefficients e4, and e5 of VO2+ and VO2+, respectively, and a single-valued parameter M. The spectra of an independent set of VIV-VV mixtures were measured experimentally and then simulated using this governing equation and the standard spectral parameters determined from the original set of mixtures. The simulated spectra were in good agreement (within less than 5%) with the measured spectra. Likewise, calibration curves for SoC were constructed using the governing equation and the standard spectral parameters. Values of SoC determined from the measured absorbance of mixtures using these calibration curves were in good agreement with the corresponding values determined from the concentrations of the parent solutions.

The governing equation, Eq. 48, and standard spectral data (Fig. 17 and the value of M) enable simulation of the spectrum of any mixture at any concentration of vanadium. They also enable determination of the SoC and overall vanadium concentration for any catholyte using absorbance measurements at a small number of wavelengths.

### Table VI. Measured absorbance and values of SoC determined from the calibration curves in Fig. 19 for mixtures in Solution Set B with a vanadium concentration of 1.581 mol dm−3. Candidate values of SoC, S = 100t, determined by Eq. 53 at each wavelength (S1,760 and S2,760 at 760 nm, and S1,660 and S2,660 at 660 nm) are shown; the true value Sφ corresponds to the candidate value (bold) that coincides at the two wavelengths; the value of S1 shown is the average. The corresponding values of SoC determined from the concentrations of the parent solutions are also shown.

<table>
<thead>
<tr>
<th>Nominal Mole Percentage of VIV</th>
<th>SoC from Parent Solutions (%)</th>
<th>Measured Absorbance (cm−1)</th>
<th>Candidate SoC (%)</th>
<th>SoC (%)</th>
<th>Deviation (%) points</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>760 nm</td>
<td>660 nm</td>
<td>S1,760</td>
<td>S2,760</td>
</tr>
<tr>
<td>5</td>
<td>94.57</td>
<td>10.36</td>
<td>10.98</td>
<td>−13.00</td>
<td>94.20</td>
</tr>
<tr>
<td>19</td>
<td>81.25</td>
<td>30.87</td>
<td>32.22</td>
<td>1.12</td>
<td>80.14</td>
</tr>
<tr>
<td>50</td>
<td>49.80</td>
<td>54.20</td>
<td>54.32</td>
<td>32.44</td>
<td>48.82</td>
</tr>
<tr>
<td>72</td>
<td>27.91</td>
<td>51.86</td>
<td>48.36</td>
<td>25.11</td>
<td>56.21</td>
</tr>
<tr>
<td>88</td>
<td>11.90</td>
<td>41.74</td>
<td>34.13</td>
<td>10.81</td>
<td>70.54</td>
</tr>
</tbody>
</table>

### Acknowledgments

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### Appendix A: Averaging φφ over Reference Concentrations

At any concentration C the average φφ(C) of the series of φφ values relative to a series of reference concentrations C1 is equal to the φφ value φφ(C) relative to the average Cφ of the reference concentrations.

\[ \bar{\phi}(C) = \frac{1}{N} \sum_{i=1}^{N} \frac{\phi(C)}{\chi(C_i)} = \frac{\chi(C)}{\chi(C_\phi)} \]  \[ [A1] \]

since \( \chi(C) \) is constant at constant C.

For any series of concentrations \( C_i \)

\[ \left( \frac{1}{\chi(C_i)} \right) \approx \frac{1}{N} \sum_{i=1}^{N} \left( \frac{1}{C_i} + C_i \right) \]

since \( \frac{1}{C_i} = \frac{1}{C} + C \) from Eq. 6. Therefore, if \( K_C \) is approximately constant,

\[ \left( \frac{1}{\chi(C)} \right) \approx \frac{1}{N} \sum_{i=1}^{N} \left( \frac{1}{C_i} + C_i \right) = \frac{1}{C} + C \]  \[ [A2] \]

where \( C \) is the average of the series of concentrations \( C_i \).


\[ \bar{\phi}(C) = \frac{\chi(C)}{\chi(C_\phi)} = \phi(C) \]  \[ [A3] \]

from Eq. 35.

### Appendix B: Changing Reference Concentrations

We show how to convert φφ from one reference concentration to another. Let \( \phi(C) \) be the value of φφ at any concentration C referenced to a concentration C1.

From Eq. 35

\[ \phi(C) = \frac{\chi(C)}{\chi(C_1)} \]  \[ [B1] \]

At a particular concentration \( C_2 \),

\[ \phi(C_2) = \frac{\chi(C_2)}{\chi(C_1)} \]  \[ [B2] \]

Dividing Eq. B1 by Eq. B2

\[ \frac{\phi(C)}{\phi(C_2)} = \frac{\chi(C)}{\chi(C_2)} = \phi(C) \]  \[ [B3] \]

where \( \phi(C) \) is referenced to \( C_2 \). Eq. B3 enables a change in reference concentration from \( C_1 \) to \( C_2 \).
We also note that

\[ \phi(C) = \frac{1}{\phi(C)} = \frac{1}{\phi(C)} . \]

### Appendix C: Generality of Eq. 42

We prove that if Eq. 42 is true for any reference concentration then it must be true with an unchanged value of \( M \) for all reference concentrations.

**Proof:**

We have shown experimentally (Fig. 15a) that Eq. 42 holds for a reference concentration \( C_r \), viz.

\[ \phi_r(C) = \frac{1 + MC_r}{1 + MC_r} \]

For any reference concentration \( C_r \),

\[ \phi_s = \frac{\phi_u(C)}{\phi_s(C)} \]

from Eq. B3 where \( C_r \) is the reference concentration for \( \phi_u \). Substituting Eq. C1 in Eq. C2

\[ \phi_s = \frac{1 + MC_s}{1 + MC_s} \]

Thus it follows that Eq. 42, which we demonstrate experimentally for \( C_r = C_m \), must then be also true for all reference concentrations. We note that \( M \) remains constant in the derivation.

### Appendix D: Concentrations and Mole Percentages in Fig. 18

Table DI lists the precise vanadium concentrations and mole percentages of \( V^{IV} \) for the solutions (Set B) in Fig. 18.

**List of Symbols**

- \( A_1 \) Measured absorbance of \( V^{IV} \) solution per unit length
- \( A_2 \) Measured absorbance of \( V^{IV} \) solution per unit length
- \( A_{ex} \) Expected absorbance per unit length
- \( A_{ex} \) Measured absorbance per unit length
- \( A_{z} \) Zero-order coefficient of SoC calibration equation Eq. 49
- \( a_1 \) First-order coefficient of SoC calibration equation Eq. 49
- \( a_2 \) Second-order coefficient of SoC calibration equation Eq. 49
- \( C \) Total vanadium concentration
- \( C_s \) Standard vanadium concentration (1 mol dm\(^{-3}\))
- \( C_r \) Average reference concentration
- \( C_t \) Reference concentration
- \( f \) Mole fraction of \( V^{II} ; f = 1 - x \)
- \( I \) Intercept of \( 1/\phi \) versus \( C \)
- \( K_1 \) Concentration equilibrium constant
- \( m \) Slope of \( A_{ex} \) versus \( f(1 - f) \)
- \( M_1 \) Negative slope of \( \phi \) versus \( C_{ex} \)
- \( M_2 \) \( \mu_{/1} \) Average of \( M_1 \) and \( M_2 \)
- \( p \) Excess absorbance parameter; \( \epsilon_{ex} \)
- \( p_1 \) \( \epsilon_{ex} \) Calculated from \( a_1(a_1 - A_{ex} - A_{ex})/C^2 \)
- \( p_2 \) \( \epsilon_{ex} \) Calculated from \( a_2(a_2 - A_{ex})/C^2 \)
- \( p_{ex} \) \( \epsilon_{ex} \) Calculated from \( 1/C_1 \)
- \( \bar{p}_{ex} \) \( \epsilon_{ex} \) Calculated from \( 1/C_2 \)
- \( \bar{p}_{ex} \) \( \epsilon_{ex} \) Calculated from \( 1/C_3 \)
- \( \lambda \) Molar extinction coefficient of \( V^{II} \)
- \( \lambda_{ex} \) Molar extinction coefficient of \( V^{II} \)
- \( \lambda_s \) Molar extinction coefficient of \( V^{II} \)
- \( \lambda_{ex} \) Molar extinction coefficient of \( V^{II} \)
- \( \lambda_{ex} \) Molar extinction coefficient of \( V^{II} \)
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