Solubility of vanadyl sulfate in concentrated sulfuric acid solutions

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Abstract

The specific energy of the vanadium redox battery is determined by the solubility of the four vanadium oxidation states in sulfuric acid. While recent studies have shown that a higher vanadium concentration than that initially proposed might be feasible, further reliable solubility data for the various vanadium ions is required if the electrolyte composition is to be properly optimized. This study describes the results of a solubility study of vanadyl sulfate in sulfuric acid. $VOSO_4$ is the species which exists in the discharged positive half-cell of the vanadium redox cell. The solubility data have been generated in sulfuric acid concentrations that range from 0 to 9 mol/l and at temperatures between 10 and 50°C. The solubility of $VOSO_4$ is found to decrease continuously with increasing H_2SO_4 concentration and decreasing temperature. At 20°C, the solubility of $VOSO_4$ in distilled water is 3.280 mol/l whereas in 9 M H_2SO_4 it is 0.260 mol/l. The drop in solubility with increasing H_2SO_4 concentration is significant and is more pronounced at lower concentrations. A multivariable solubility prediction model has been developed as a function of temperature and total sulfate/bisulfate (SO_4^{2-} and HSO_4^-) concentration using the extended Debye–Huckel functional form. The average absolute deviation of the predicted solubility values from experimental data is 4.5% with a maximum deviation of about 12% over the abovementioned temperature and sulfuric acid concentration range. When solubility data in the more useful H_2SO_4 concentration range of 3–7 M is considered, the solubility correlation improved with an average absolute deviation of only 3.0% and a maximum deviation of about 7%. © 1998 Elsevier Science S.A.

Keywords: Vanadium redox battery; Sulfuric acid concentration; Vanadyl sulfate; Solubility

1. Introduction

Solubility data of vanadium compounds are of considerable interest for the All Vanadium Redox Flow Battery (AVRFB). The AVRFB pioneered and currently under development at The University of New South Wales, [1–4] is showing great promise as an efficient new energy-storage system for a wide range of applications. In this cell, the electrolyte is one of the most important components; it is not only the conductor of the ions, but is also the energy-storage medium. The cell employs V(III)/V(II) and V(V)/V(IV) redox couples in the negative and the positive half-cells, respectively. The power outlet of the system is determined by the size of the battery stack, while the capacity is set by the volume of the electrolytes in the tanks.

Earlier studies [3–5] suggested that 2 M V(IV) in 3–4 M H_2SO_4 could be safely employed in applications where the battery undergoes continuous cycling. Precipitation of V(II), V(III) and V(IV) ions from 2 M vanadium solutions

is observed at temperatures below about 10°C whereas V(V) solution precipitates above 40°C. The precipitation of various vanadium species occur during the battery operation and depends on the solubility limits and induction times. Once precipitation begins, it continues until stability has been achieved. Higher sulfuric acid concentration favours the precipitation of V(II), V(III) and V(IV) ions, but stabilizes V(V) ions [5,6]. Precipitation can be eliminated over a wider temperature range by reducing the vanadium concentration below 2 M. While concentrations as low as 1.5 M are acceptable for stationary applications, however, a minimum vanadium concentration of 3 M is required to make the vanadium battery suitable for electric vehicles.

To determine the optimum conditions of H_2SO_4 concentration and temperature where all the vanadium species are most stable, the solubility of these compounds has been studied systematically. Such studies are required since reliable solubility data which permit determination of the degree of supersaturation and prediction of the precipitation of vanadium species are not readily available in the literature. This communication presents the results of a solubility study of vanadyl sulfate ($VOSO_4$) over a wider

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range of H_2SO_4 concentrations, from 0 to 9 mol/l, and at temperatures from 10 to 50°C.

2. Experimental procedure

A solution saturated with a given solute is one that is in equilibrium with the solid phase and it is the achievement of true equilibrium that presents one of the biggest difficulties. To achieve equilibrium saturation, prolonged and intimate contact is required between excess solid and solution at a constant temperature for several hours or, in certain cases, many days [7].

Sample glass bottles of size 40 ml capacity with teflon stoppers containing sulfuric acid of desired concentration in the range of 0–9 M were brought to a constant temperature of the desired value (10–50°C) in the water bath. An immersion circulator (Thermoline) capable of controlling temperature to an accuracy of ± 0.5°C was used to maintain the constant temperature. Solids of reagent grade $VOSO_4 \cdot 5H_2O$ from Aldrich Chemicals were added in sufficient quantity so that excess solids remained when the system reached equilibrium. Preliminary experiments indicated that the equilibration time for the $VOSO_4$–H_2SO_4 system is about 10–12 days. Nevertheless, shaking of the bottles was carried out on daily basis for about 45 days. Equilibrium was thus achieved from the unsaturated state [8,9].

Liquid samples were collected after keeping the solution for about 3 days without shaking so that the fine particles could settle completely. A membrane filter (Millipore ready-to-use filters in plastic assembly) of size 0.45 μm and a plastic syringe was used to collect the liquid samples which were diluted to the desired level in distilled water. The liquid samples were then analysed using inductively coupled plasma (ICP, Labtam, Australia) to determine the equilibrium concentration of vanadyl ion (VO^{2+}) and total sulfur (SO_4^{2-} and HSO_4^-). Calibration of the ICP instrument was done periodically and a calibration curve was developed to accommodate any drift in the instrument. The solid phase from a few, selected experiments was analysed by XRD and it compared very well with that of the pure $VOSO_4 \cdot 5H_2O$ used in these experiments.

3. Results and discussion

The saturation concentration of $VOSO_4$ in the samples was determined at 10, 20, 30, 40 and 50°C in sulfuric acid concentrations which ranged from 0 to 9 M. The saturation concentrations of total vanadium and total sulfur (SO_4^{2-} and HSO_4^-), as obtained from ICP, are listed in Table 1. The solubility of $VOSO_4$ as a function of total sulfur ($SO_4^{2-} + HSO_4^-$) at equilibrium is presented in graphical form in Fig. 1 and the variation in solubility with initial sulfuric acid concentration is shown in Fig. 2. In order to
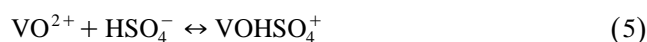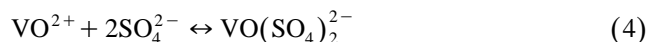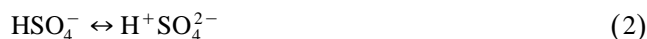
Table 1
Solubility of vanadyl sulfate ($VOSO_4$) in various sulfuric acid concentrations at temperatures from 10 to 50°C

Initial H_2SO_4 (mol/l)	Temp (°C)	At equilibrium		
		Total sulfur[a] (mol/l)	$VOSO_4^a$ (mol/l)	K_{SIP} (M)
0.0	10.0	3.167	3.037	9.618
1.0	10.0	3.659	2.432	8.899
3.0	10.0	4.692	1.448	6.794
5.0	10.0	5.987	0.784	4.694
6.0	10.0	6.895	0.493	3.399
7.0	10.0	7.390	0.384	2.838
8.0	10.0	8.219	0.243	1.997
9.0	10.0	8.802	0.185	1.628
0.0	20.0	3.449	3.280	11.313
3.0	20.0	4.717	1.786	8.425
5.0	20.0	6.129	0.995	6.098
6.0	20.0	6.925	0.711	4.924
7.0	20.0	7.434	0.570	4.237
8.0	20.0	8.328	0.363	3.023
9.0	20.0	8.936	0.260	2.323
0.0	30.0	3.720	3.640	13.541
3.0	30.0	4.939	2.149	10.614
5.0	30.0	6.374	1.262	8.044
6.0	30.0	6.868	0.997	6.847
7.0	30.0	7.724	0.718	5.546
8.0	30.0	8.404	0.514	4.320
9.0	30.0	9.291	0.386	3.586
0.0	40.0	4.105	3.994	16.395
3.0	40.0	5.353	2.460	13.168
5.0	40.0	6.454	1.585	10.230
6.0	40.0	7.178	1.216	8.728
7.0	40.0	7.851	0.875	6.869
8.0	40.0	8.510	0.676	5.753
9.0	40.0	9.347	0.492	4.599
0.0	50.0	4.458	4.349	19.388
3.0	50.0	5.598	2.822	15.798
5.0	50.0	6.510	1.904	12.395
6.0	50.0	7.271	1.474	10.718
7.0	50.0	7.938	1.023	8.121
8.0	50.0	8.665	0.778	6.741
9.0	50.0	9.407	0.586	5.513

[a]Saturation concentration at equilibrium.

calculate the solubility product of $VOSO_4$, it is necessary to determine the equilibrium concentrations of VO^{2+} and SO_4^{2-}. Unfortunately, neither ICP nor ion chromatography (IC) is able to distinguish between the SO_4^{2-} and HSO_4^- in the solution.

Furthermore, the chemistry of vanadium is complex—a large number of different species exist at different potentials and pH values. Ivakin and Voronova [10] have suggested that the following reactions can occur:
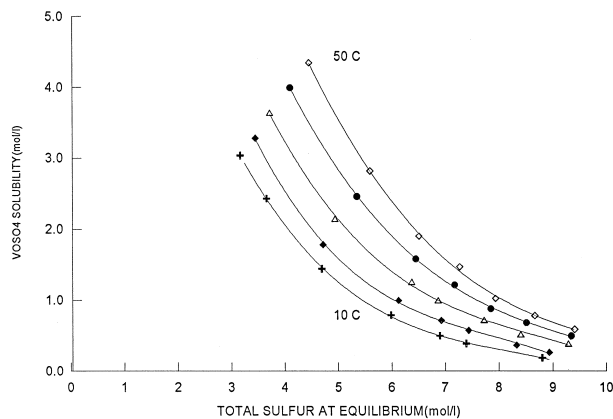
$$VOSO_4 \cdot xH_2O \leftrightarrow VO^{2+} + SO_4^{2-} + xH_2O \qquad (1)$$

$$HSO_4^- \leftrightarrow H^+SO_4^{2-} \qquad (2)$$

$$VO^{2+} + SO_4^{2-} \leftrightarrow VOSO_4^0 \qquad (3)$$

$$VO^{2+} + 2SO_4^{2-} \leftrightarrow VO(SO_4)_2^{2-} \qquad (4)$$

$$VO^{2+} + HSO_4^- \leftrightarrow VOHSO_4^+ \qquad (5)$$

Fig. 1. Variation in solubility of $VOSO_4$ with concentration of total sulfur at equilibrium.

The same authors calculated the stability constants of Eqs. (3)–(5) as 55 ± 3, 320 ± 10 and 1.7 ± 0.3, respectively. Based on the experimental results, it was concluded that vanadium (IV) complexes do exist but are relatively unstable. Strehlow and Wendt [11] reported the association constant of the ion-pair $VOSO_4^0$ in distilled water as 300. There exist discrepancies and uncertainties in the reported equilibrium constants of vanadium (IV) ions and sulfate ions, and because of the lack of availability of reliable data, it is not possible to calculate accurately the distribution of the various species and thus, the, solubility product (K_{sp}) of $VOSO_4$.

An attempt was made to calculate the solubility product (K_{sp}) of vanadyl sulfate by considering reactions 1 and 2 according to the procedure outlined by Marshall and Jones [12] for the determination of K_{sp} for gypsum in sulfuric acid solutions. These authors ignored the contribution of gypsum concentration to the density of the solution and assumed that the density of sulfuric acid is equivalent to the density of the solution of gypsum and sulfuric acid. A set of mass action equations was then solved iteratively to determine the K_{sp}, the second dissociation constant of H_2SO_4 (K_2) and the ionic strength of the system (I). In
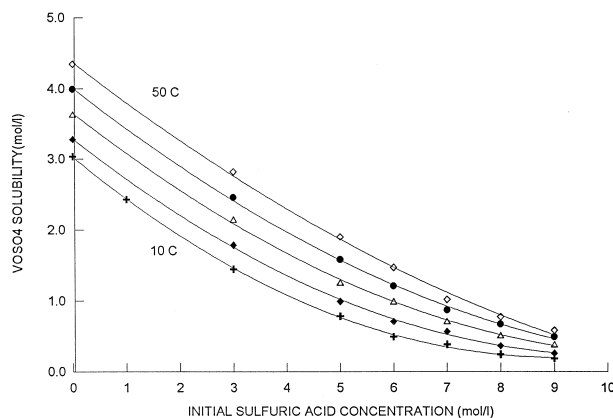
the present system, however, the solubility of $VOSO_4$ is fairly high. Thus, its contribution to the density cannot be ignored and a K_{sp} calculation cannot be performed.

In view of the abovementioned difficulties for calculating the K_{sp}, the term K_{sp} was replaced in this study by a new parameter, 'saturation ionic product (K_{SIP})' defined as:

$$(K_{SIP}) = [VO^{2+}]^* ([SO_4^{2-}] + [HSO_4^-]) \qquad (6)$$

The K_{SIP} data are included in Table 1 along with the solubility data. Although it has no theoretical significance, it is believed that the saturation ionic product (K_{SIP}) will be of more practical utility. Thus, to determine the degree of supersaturation or scaling potential of a given vanadium solution, the ionic product (K_{IP}) of total vanadium and total sulfur of the solution (obtained from ICP), can be compared with the saturation ionic product (K_{SIP}).

To discuss the experimental results, the following assumptions are made: (i) the first dissociation constant of H_2SO_4 is infinite which means that there are no neutral H_2SO_4 species; and (ii) the vanadium (IV) and sulfate/bisulfate ion complexes are unstable and result in unassociated vanadium (IV) ions.

The results in Fig. 1 show that the solubility of $VOSO_4$ decreases continuously with increasing H_2SO_4 concentration and decreasing temperature. The effect of H_2SO_4 concentration on $VOSO_4$ solubility is more pronounced at lower concentrations. The decrease in solubility is greater in the H_2SO_4 concentration range 0–7 M, and at 8 and 9 M H_2SO_4 concentration, the rate of decrease in solubility is minor. The higher rate of decrease in solubility at lower sulfuric acid concentration may be due to a higher dissociation of bisulfate ions to sulfate ions which shifts the equilibrium towards the left in Eq. (1) and, thereby, results in a faster drop in solubility. As the sulfuric acid becomes more concentrated, the dissociation of bisulfate ions becomes less [12,13] and thus reduces the rate of decrease in
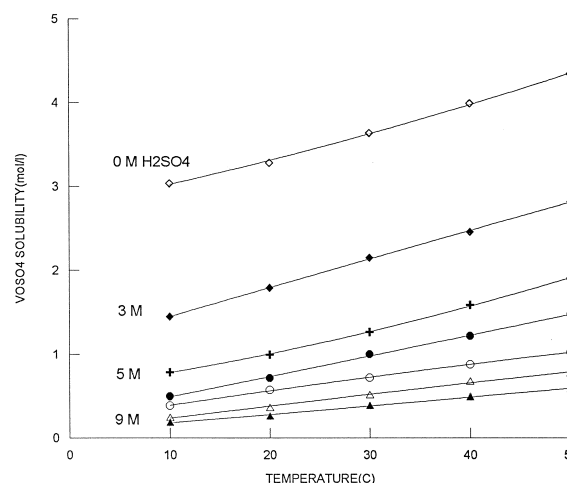

Fig. 2. Variation in solubility of $VOSO_4$ with initial concentration of sulfuric acid.

Fig. 3. Effect of temperature on solubility of $VOSO_4$ in various sulfuric acid concentrations.
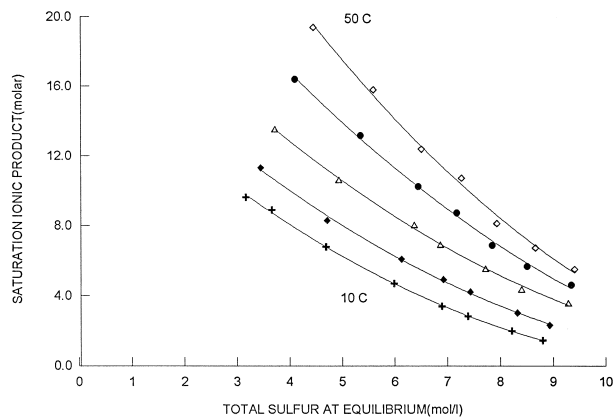
Fig. 4. Saturation ionic product (K_{SIP}) of $VOSO_4$ as a function of total sulfur concentration at equilibrium.

VOSO$_4$ solubility. The experimental results of the present study confirm the findings of Ivakin and Voronova [10] that vanadium (IV) ions and sulfate complexes are unstable, otherwise the solubility of $VOSO_4$ would have increased to a certain extent with increasing H_2SO_4 concentration.

The effect of temperature on the solubility of $VOSO_4$ is given in Fig. 3. The solubility increases with temperature and the effect is more significant at lower H_2SO_4 concentrations. This could be due to the fact that the second dissociation constant (K_2) of H_2SO_4 decreases sharply with rising temperature [12] and, thereby, would cause a reduction of SO_4^{2-} ions and thus allow the solubility of $VOSO_4$ to increase.

The variation in saturation ionic product (K_{SIP}) with total sulfur at equilibrium is shown in Fig. 4. The relationship is almost linear. This behaviour indicates a rapid increase in precipitation potential with increase in vanadium as well as in sulfuric acid concentration.

3.1. Solubility prediction models

If reliable solubility data are available, solubility correlations can be developed using the Extended Debye–Huckel equation either directly or with modification by introducing additional constants. The solubility correlations will assist the prediction of the solubilities of vanadium species for desired sulfuric acid concentration and temperature. Marshall et al. [14] determined solubility data of various forms of $CaSO_4$ (including gypsum) in NaCl solutions at various temperatures. The following relationship was used to correlate the gypsum data:

$$\log K_{sp} = \log K_{sp}^0 + 8A\sqrt{I}/(1 + Ba\sqrt{I})$$
$$+ 2CI + 2DI^2 \qquad (7)$$

Ostroff and Metler [15] presented gypsum solubility data in a mixture of $NaCl + MgCl_2$ at temperatures be-

tween 28 and 90°C. The data was correlated using the following regression equation:

$$S = A + B(mn) + C(mn)^2 + D(mn)^3 + E(mn)^4 \qquad (8)$$

where S = gypsum solubility; m = concentration of $MgCl_2$ in the mixture (molal); n = concentration of NaCl in the mixture (molal); A, B, C, D, E = regression constants.

Eq. (7) can also be used with minor modifications to develop solubility correlations for the vanadium compounds and the constant (C, D) can be estimated by a Statistical Analysis System (SAS). After screening different modified relationships, the following equation was found to provide the best representation of the vanadyl sulfate data.

$$\log S = C1 + C2/T + C3 {}^* T + C4\sqrt{m_s}/(1 + C5\sqrt{m_s})$$
$$+ C6m_s^{1/3} + C7 {}^* T/m_s \qquad (9)$$

where S = solubility of vanadyl sulfate (M); m_s = total sulfur concentration (SO_4^{2-} and HSO_4^-) in mol/l; T = temperature (°C); $C1$–$C7$ = regression constants.

The constants $C1$–$C7$ estimated after carrying out regression analysis using SAS are listed in Table 2 and includes all the 36 data points generated in this study. The average deviation obtained was 2about 4.5% and the maximum deviation was 12.0%. This maximum deviation was observed at conditions of 9 M H_2SO_4 concentration and 10°C. Relatively high deviations were also observed mostly at an acid concentration of 9 M concentration and other temperatures. An improved correlation was therefore developed using Eq. (9) but considering the sulfuric acid concentration range 3–7 M which is of more practical utility. The resulting regression constants $C1$–$C7$ are given in Table 2. The average deviation was 3.0% with a maximum deviation of only 6.7%

Regression analyses were also performed on the saturation ionic product (K_{SIP}) as defined in Eq. (6). The functional form which was used to model the solubility data was also found suitable for correlating saturation ionic product (K_{SIP}) data and is represented as a function of total sulfur concentration and temperature in the following manner:

$$\log K_{SIP} = C1 + C2/T + C3 {}^* T + C4\sqrt{m_s}/(1 + C5\sqrt{m_s})$$
$$+ C6m_s^{1/3} + C7 {}^* T/m_s \qquad (10)$$

where K_{SIP} = saturation ionic product (M); m_s = total sulfur concentration (SO_4^{2-} and HSO_4^-) in mol/l; T = temperature (°C); $C1$–$C7$ = regression constants.

The regression constants $C1$–$C7$ for saturation ionic product (K_{SIP}) correlation are given in Table 2 and the average absolute deviation and maximum deviation are 4.0 and 12.6%, respectively. When regression was performed using K_{SIP} data in 3–7 M H_2SO_4 concentration, the average absolute deviation dropped again to 3.0% with a maximum deviation of 7.1%. The correlation coefficient in all four cases was excellent at about 0.99.

Table 2
Regression constants of solubility correlations and ionic product correlations

Regression constants	Solubility correlations (initial H_2SO_4 concentration range)		Equivalent ionic product correlations (initial H_2SO_4 concentration range)	
	0–9 M	3–7 M	0–9 M	3–7 M
$C1$	−0.45	−4.33	0.454	−5.55
$C2$	0.017	0.017	0.017	0.017
$C3$	−1.2	−1.0	−1.2	−1.0
$C4$	11.63	19.76	8.265	21.58
$C5$	1.33	0.84	0.5	0.83
$C6$	−3.5	−6.39	−4.89	−6.169
$C7$	−0.04	−0.04	−0.04	−0.0406
No. of data points	36	20	36	20
Mean deviation (%)	4.5	3.0	4.0	3.1
Max. deviation (%)	12.1	6.7	12.6	7.1
Corr. coeff. (R^2)	0.999	0.999	0.996	0.998

To predict the scaling tendencies or precipitation potential of a supersaturated vanadium (IV) solution to be used in the battery, a scaling index has been defined as follows:

$$\text{Vanadium Scaling Index (VSI)} = K_{IP}/K_{SIP} \qquad (11)$$

where VSI = 1 solution is saturated; VSI < 1 solution is undersaturated; VSI > 1 solution is supersaturated (scaling possible); K_{IP} = product of total vanadium (VO^{2+}) and total sulfur (SO_4^{2-} and HSO_4^-) concentration of a given solution at a particular temperature (obtained from the analysis of the solution by ICP); K_{SIP} = product of total saturation vanadium VO^{2+} and total sulfur (SO_4^{2-} and HSO_{4-}) concentration at equilibrium at the same temperature (from Eq. (10)).

If temperature and composition in terms of the total vanadium and total sulfur of a supersaturated vanadium (IV) solution can be analysed by ICP, then at any desired temperature (between 10–50°C) the scaling tendencies can be predicted using Eqs. (10) and (11). If the value of VSI is unity or less than unity, a scale will not form. If VSI is greater than unity then the solution has the potential to form a scale, but the start of precipitation will depend on the induction period of that solution and the speed at which it will precipitate depends on the kinetics. The potential for scaling can thus be predicted from VSI by using the K_{SIP} correlation.

4. Conclusions

The solubility data of vanadyl sulfate has been generated in sulfuric acid of concentration 0 to 9 M and over the temperature range 10–50°C. The effect of both sulfuric acid concentration and temperature on the solubility of vanadyl sulfate is significant. The rate of increase of solubility with acid concentration decreases at high concentrations. Similarly, the increase in solubility with increasing temperature is more pronounced at lower H_2SO_4 concentrations. The variation in solubility is linked strongly with the second dissociation constant of H_2SO_4 at different temperatures and sulfuric acid concentrations.

The solubility data and saturation ionic product (K_{SIP}) data of vanadyl sulfate are correlated using the Extended Debye–Huckel functional form. For a sulfuric acid concentration range of 0–9 M and a temperature range 10–50°C, the average absolute deviation is < 4.5%, whereas if selected solubility data points are taken in the more useful sulfuric concentration range of 3–7 M, the average absolute deviation is ∼ 3%. A vanadium scaling index (VSI) has been defined to predict scaling tendencies of supersaturated V(IV) solutions using a saturation ionic product (K_{SIP}) correlation. Similar analyses are being undertaken for other vanadium oxidation states that occur during charge–discharge cycling of the vanadium redox battery so that precipitation tendencies in the vanadium electrolyte can be predicted accurately and the electrolyte composition can be properly optimized for a range of vanadium battery applications.

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