A Closer Look into Solubility in the Binary NaVO₃–H₂O and NH₄VO₃–H₂O Systems from 298.15 to 333.15 K and 0.1 MPa

Mikael A. E. Manninen,* Tuomas J. Vielma, and Ulla M. Lassi

ABSTRACT: The solubilities of anhydrous sodium metavanadate (NaVO₃), its hydrated form (NaVO₃·2H₂O), and ammonium metavanadate (NH₄VO₃) in water were measured in the temperature range from 298.15 to 333.15 K using the isothermal saturation method. Previous literature data on the solubility in these binary systems were surveyed, and its reliability was evaluated. Empirical equations were fitted to the accepted data to obtain analytical expressions for the solubilities of the three salts as functions of temperature. Only a few previous papers, mostly published over 60 years ago, were found to report experimental points on the solubility curve of the dihydrate NaVO₃·2H₂O. We herein report new experimental determinations of the dihydrate solubility. Finally, it was investigated whether the solubility of NH₄VO₃ at 298.15 K can be predicted using only thermodynamic data appearing in the literature. Although there seems to be a consensus on the identity of the major species in dilute V(V) solutions, discrepancies in the values of infinite dilution equilibrium constants (I = 0) exist. Accordingly, the solubilities predicted using different sets of equilibrium constants were somewhat scattered but of approximately correct magnitude. The neglect of ion-pair/complex formation and the lack of an accurate model for the activity coefficients are probably the most serious flaws limiting the accuracy of the current models. It is clear that much work remains to be done if temperature-dependent thermodynamic models extending to high vanadium concentrations are to be developed.

1. INTRODUCTION

Since its discovery in the early 19th century, many investigators have been fascinated by the diverse chemistry of vanadium (V). During the years, it has found many important applications, especially in the steel, battery, and medical industries. As vanadium concentrations in natural minerals are usually low, the production of vanadium from primary raw materials is not often economically feasible. At the same time, industrial operators are seeking ways to alter their operations to comply with the principles of circular economy. Consequently, the recovery of vanadium from secondary raw materials, such as steel industry slags, has received increased attention in the recent years.

Modern vanadium recovery processes rely much on hydrometallurgical unit operations. Thermodynamic models for aqueous vanadium solutions could therefore find widespread application in the design and control of such processes. Unfortunately, there is currently a lack of accurate data for the thermodynamic properties of aqueous vanadium solutions. Although considerable efforts have been made to determine the identity and the formation constants of the species existing in aqueous V(V) solutions, these studies have been limited to low V concentrations (<0.3 mol/kg). The experimental data available for concentrated solutions include mostly solubilities and densities for a number of binary, ternary, and quaternary systems containing NaVO₃ and/or NH₄VO₃ as a component. A notable portion of the above data comes from the works of Trypuč and co-workers and most of the above publications report only a few experimental points for the binary systems. Also, it seems that the existence of two solid forms of NaVO₃ in the stability region of liquid water has practically been omitted in the more recent solubility studies although discovered already by McAdam and Pierle over a hundred years ago. Clearly, a demand for systematic studies on these systems still exists.

The principal objective of the present work was to determine, as accurately as possible, the solubilities of NaVO₃, NaVO₃·2H₂O, and NH₄VO₃ in water and the respective uncertainties at temperatures within the stability region of the liquid phase at atmospheric pressure, which is the region of interest in most hydrometallurgical applications. Solubility determinations were conducted in the range of 298.15–333.15 K with an apparatus designed specifically for the measurement of solubilities. The guidelines outlined by Königsberger have been followed throughout the work. The uncertainties associated with the measured solubilities have been estimated following the

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Table 1. Sample Sources and Purities

<table>
<thead>
<tr>
<th>chemical name</th>
<th>CAS RN</th>
<th>M/(g/mol)</th>
<th>source</th>
<th>mass fraction purity</th>
<th>purification method</th>
</tr>
</thead>
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<tr>
<td>sodium metavanadate</td>
<td>13,718–26-8</td>
<td>121.929</td>
<td>Merck</td>
<td>≥0.98</td>
<td>none/filteringc</td>
</tr>
<tr>
<td>ammonium metavanadate</td>
<td>7803-55-6</td>
<td>116.978</td>
<td>Fisher Scientific</td>
<td>≥0.995</td>
<td>none</td>
</tr>
<tr>
<td>EDTANa2·2H2O</td>
<td>6381-92-6</td>
<td>372.238</td>
<td>Merck</td>
<td>0.99–1.01</td>
<td>drying at 80 °Cf</td>
</tr>
<tr>
<td>sodium chloride</td>
<td>7647-14-5</td>
<td>58.440</td>
<td>Baker</td>
<td>≥0.995</td>
<td>none</td>
</tr>
<tr>
<td>ZnSO4·7H2O</td>
<td>7446-20-0</td>
<td>287.541</td>
<td>Merck</td>
<td>≥0.995</td>
<td>none</td>
</tr>
</tbody>
</table>

“Ethylenediamine-tetraacetic acid disodium salt dihydrate. Stoichiometric dihydrate should be obtained by drying at 80 °C for 4 days. The solid was used as received, but the stock solution was passed through a 0.45 μm membrane.

2. MATERIALS AND METHODS

2.1. Materials. Details of the samples used in this work are given in Table 1. A stock solution of sodium metavanadate was prepared by dissolving the anhydrous salt in ultrapure water (Milli-Q water purification system). The solution was then passed through a 0.45 μm membrane filter to remove any insoluble impurities. Ammonium metavanadate was used directly without further purification. A 0.01 mol/kg EDTA (ethylenediamine-tetraacetic acid) solution was prepared, following Schwarzenbach and Flaschka, by dissolving 3.7225(12) g of Na2EDTA·2H2O (dried 4 days at 80 °C) in 999.7(3) g ultrapure water. The solution was left to stand for 24 h to ensure complete dissolution, after which it was passed through a 0.45 μm membrane and stored in plastic bottles sealed with parafilm. The EDTA concentration was checked against a standard solution of NaVO3·2H2O, 2.165 g cm⁻³ for NaCl, 1.01 g cm⁻³ for Na2EDTA·2H2O, 0.998207 g cm⁻³ for H2O, and 0.0012041 g cm⁻³ for air. All molar masses used in this work were calculated from the 2021 IUPAC standard atomic weights.

2.2. Analytical Methods. The V(IV) concentrations in the samples were measured using two independent methods: evaporative gravimetry and EDTA titration. The NH4VO3 solutions were analyzed only by titration, since the gravimetric analysis of such dilute solutions would have required inconveniently large sample volumes. The concentration of NaCl was determined gravimetrically with the same procedure as given below, except that heating to 500 °C was required to completely remove all occluded water. All heating and drying operations in this work were conducted under atmospheric pressure.

The procedure for the evaporative gravimetry is given as follows: 3–5 mL of the NaVO3 solution was transferred to a preweighed crucible. The samples were evaporated to dryness on a hot plate at subboiling temperature followed by heating at 400 °C for 24–48 h, and weighing the crucibles containing the residues. A few residue samples were combined and analyzed by XRD, which identified the residues as α-NaVO3 (see SI). An empty crucible was carried through the whole procedure and weighed before and after all weighing sessions to correct for effects such as adsorbed moisture. The density of the analyzed solution required in the buoyancy correction was estimated from the measured weight and volume of the sample. All measurements were made at least in duplicate. The average relative standard deviation for 57 samples of NaVO3 molality within 0.26–0.98 mol/kg was 0.14%.

The procedure for the EDTA titration was adopted from Schwarzenbach and Flaschka, but a slight modification was found necessary. If the blue solution of V(IV) was boiled as advised by Schwarzenbach and Flaschka, it turned green suggesting the presence of V(III). The titration of the boiled solution was not possible, since soon after the titration was begun, a yellow/orange color developed, which sluggishly reverted to red. Therefore, the solution was not boiled after the reduction. The procedure is given as follows: A weighed sample of vanadium (V) solution containing 2–10 mg V was added to a flask with 50 mL of ultrapure H2O and 10 mL of ~0.9 M acetate buffer (pH = 4.57). About 0.2–0.25 g of i-ascorbic acid was added to reduce V(V) to V(IV) turning the solution from yellow to blue. A pinch of Cu-PAN indicator was added and the solution stirred vigorously until a violet color developed. The solution was heated to ca. 30–50 °C and 0.01 mol/kg EDTA was added from a syringe until a color change from violet to bright yellow. The endpoint was taken to have been reached when the yellow color persisted for at least 10 min. The amount of consumed titrant was measured by weighing the syringe before and after the titration. Approximate density of 1 g cm⁻³ was used in the buoyancy correction for weighing the EDTA and NaVO3.
than 0.3%. The precision
was slightly better for the more dilute NH₄VO₃ solutions, with an average standard deviation of 0.23% for 13 samples of
molality within 0.01–0.04 mol/kg. As a further validity check,
three 2 mL aliquots of a 1001.5(40) mg L⁻¹ V(IV) certified
standard solution were titrated with the above method with
recoveries of 99.90, 99.26, and 100.46%.

2.3. Solubility Measurements. The solubility apparatus
(Figure S10) consisted of a large glass walled tank filled with
deionized water and equipped with a slowly rotating syringe
stand. Plastic syringes with Luer–Lock tips (SS50L1, Terumo)
were used to contain the samples. The design of the apparatus
closely followed that described by Capewell et al. This design
allows sampling to be conducted fully immersed in the bath,
which minimizes any errors related to temperature gradients
during sampling. Another advantage of the method is that no
mechanical stirring is needed in the sample vials, which could
cause attrition or secondary nucleation of the sample crystals.
The temperature of the bath was monitored by two platinum
resistance thermometers positioned in different sides of the
bath. The output of the sensor near the copper heating element
was used to automatically adjust the power supplied to the
element. A third thermometer (calibration traceable to ITS-90
with accuracy ±0.009 K, Traceable Products, Webster, Texas,
USA) was used to fine-tune the temperature of the bath and to
provide a validity check for the temperature. The 24 and 1 h
average temperatures of the bath remained within less than ±3
and ±7 mK from the target temperature at 298.15 K,
respectively. The average difference between the maximum
and minimum temperatures recorded within one hour was 12
mK, and the maximum difference during the whole 72 h
monitoring period was 19.2 mK. For higher temperatures, the
absolute deviations were slightly larger, but still so small that the
error in the measured solubility due to this effect was negligible
compared to the total uncertainty of the solubility measurement
(see SI).

2.4. Analysis of the Solid Phase. In the case of the
NaVO₃-H₂O system, there were clearly two distinct solid
phases, which had a region of stability in the studied temperature
range. Supposedly, these phases were anhydrous NaVO₃ and
dihydrate NaVO₃·2H₂O. The crystals of the dihydrate were larger than those of the anhydrous salt, and the dihydrate
solubility had a much steeper temperature dependence. The
initial solid NaVO₃ was analyzed by XRD, and it was identified
to be anhydrous NaVO₃ (see SI). Under ambient pressure, the
dihydrate loses its water of crystallization already at 305–307 K,
and the dehydration has been reported to occur just by placing
the sample in a desiccator. This fact complicates the characterization of the solid phase in equilibrium studies by
techniques such as XRD, since even gentle drying and grinding
could cause the hydrate to lose its water of crystallization.

To provide some verification that the phase under study was
in fact the NaVO₃·2H₂O, the “wet residue” method of
Schreinemakers was employed. A small amount of NaCl in
the syringe containing the investigated solid phase and H₂O. The mixture was allowed to equilibrate, and a sample
was withdrawn from the solution phase as in an ordinary
solubility determination. The vanadium concentration in the
sample was measured by duplicate titrations with EDTA.
Another aliquot of the sample was analyzed by evaporative

gravimetry. The solid residue remaining in the crucibles was
assumed to be a mixture of NaCl and NaVO₃. By subtracting
the mass of NaVO₃ from the total mass of the residue, the amount of
NaCl in the residue, and subsequently, its mole fraction in
the original sample was obtained. Right after taking the sample from the
solution phase, the solid in the sample syringe was separated from
the majority of the remaining solution, dissolved in a
known amount of water, and analyzed as above.

If it is assumed, that all the NaCl was in the solution, the
amount of NaCl in the wet residue sample gives a measure of the
saturated solution retained by the wet residue. If the mole
fraction compositions of the two mixtures (saturated solution
and the wet residue) are now plotted on a ternary composition
diagram, the tie line connecting these two points should cross
the NaVO₃-H₂O axis at the point corresponding to the
composition of the solid in equilibrium with the saturated
solution. However, the accurate determination of the intercept is
rather difficult due to the small angle in which the line
approaches the axis. Our results show an intercept of 0.61, which
corresponds to the formula NaVO₃·1.5H₂O. At the 95%
confidence level, the intercept lies between 0.48 and 0.68, which
correspond to 0.92 and 2.13 water molecules in the formula. A
plot illustrating the results is shown in Figure S6.

2.5. Fitting Equations. In principle, it is possible to derive an
expression for the temperature dependency of the solubility
based on general thermodynamic considerations. However, this
requires knowledge on the activity coefficients of the dissolved
species, which often is not available. This is also the case for the
present systems. Therefore, an empirical expression was adopted
to correlate the data. The used equation has, however, some
basis in thermodynamics and is of the following form:

\[
Y(T) = A_0 + A_1 \left( \frac{T}{T_r} \right) + A_2 \ln \left( \frac{T}{T_r} \right) + A_3 \left( \frac{T}{T_r} \right)^2 + \cdots
\]

(1)

where

\[
Y(T) = \ln \left( \frac{x^2(1-x)^y(2+r)(2+r)}{r(1+x)^{(2+r)}} \right)
\]

(2)

and \(x\) is the mole fraction of the solute in the saturated solution, \(r\)
is the number of water molecules in the formula of a hydrated
salt, \(T\) is temperature in K, and \(T_r\) is an arbitrary reference
temperature. We have adopted \(T_r = 298.15\) K as it makes the
regression parameters in eq 1 to be of convenient magnitude.

A justification for the form of eq 1 has been given by Lorimer
and Cohen-Adad, who have shown that the parameters of eq 1
are loosely connected to the standard enthalpy, entropy and heat
capacity change of solution at the reference temperature (and
pressure). However, the contributions of excess terms, arising
from the nonideality of the solution, have also been incorporated
in the parameters of eq 1, which makes their physical
interpretation ambiguous. Even if the activity coefficients
along the whole solubility–temperature curve were known,
the calculation of thermodynamic quantities from the values of
the parameters could be infeasible due to the uncertainties of the
parameters and the correlations between them. Therefore,
the purpose of eq 1 is only to represent the current solubility data in
a readily applicable analytical form.

Parameter optimization was conducted in MATLAB
by the method of weighted least squares. The smallest uncertainty in \(Y\)
divided by the standard uncertainties of the datapoints were
used to weight the data, so that the point with the smallest uncertainty got a weight of 1. The standard uncertainty in \( m \) propagated to \( Y \) was estimated as:

\[
\frac{u(Y)}{dY} = \frac{u(x_i)}{dx}
\]

(3)

\[
\frac{u(x_i)}{dx} = \frac{u(m_i)}{dm}
\]

(4)

where \( u(Y), u(x_i), \) and \( u(m_i) \) are the respective uncertainties in \( Y, x_i \) and \( m \) of datapoint \( i \). The uncertainty in \( T \) was assumed to be negligible for the purposes of the regression analysis.

### 3. RESULTS AND DISCUSSION

#### 3.1. Validation of the Experimental Procedures

A few solubility determinations for NaCl and ZnSO\(_4\)·7H\(_2\)O were made to validate the used procedures. The solubility of NaCl at 298.15 K estimated from duplicate samples was 6.139(4) mol/kg. Hefter\(^{34} \) suggests a value of 6.153(5) mol/kg\(^{34} \) and the value recommended in the IUPAC solubility data series\(^{35} \) is 6.156(24) mol/kg (uncertainties correspond to one standard deviation). Table 2 shows how the results of the present work compare to the recommended values in the IUPAC review at three temperatures. The agreement was considered reasonable, given that the values at 298.15 K accepted in the IUPAC review show a spread of about 0.117 mol/kg and a standard deviation of 0.024 mol/kg.

The concentration of Zn(II) in the equilibrated samples containing ZnSO\(_4\)·7H\(_2\)O and water was measured by titration with EDTA. The average of duplicate determinations at 298.15 K was 3.535(4) mol/kg, whereas the value determined in the isopiestic studies of Albright and co-workers\(^{47} \) is 3.554(7) mol/kg. This was considered to be a reasonably good agreement.

#### 3.2. Attainment of Equilibrium

In order to produce reliable solubility data, verification on the attainment of equilibrium is essential. A long time was required to reach equilibrium, especially in the case of the NaVO\(_3\)·H\(_2\)O system. A discontinuity in the slope of the solubility curve of NaVO\(_3\) near 308 K indicated a solid phase transformation, whereas only one stable solid was observed for NH\(_3\)VO\(_3\). To confirm the attainment of equilibrium, it was investigated if approaching the equilibrium from under- or supersaturation affected the results. Changes in the composition of the NaVO\(_3\)·H\(_2\)O system with time were also monitored to provide some perception about the time required to reach the equilibrium.

The samples of NaVO\(_3\)·2H\(_2\)O were prepared by allowing it to precipitate in the sample syringes at room temperature, using the commercial anhydrous NaVO\(_3\) as the starting material. It was observed that when a sample of the undried NaVO\(_3\) was placed in contact with an aqueous solution, the solid slowly converted to the less soluble form (dihydrate) upon standing at room temperature within a few days or weeks (Figure 1a). However, if NaVO\(_3\) was dried at 105 °C and stored in a desiccator before preparing the sample, the precipitation of the dihydrate did not occur at least within five days. A mass loss of 0.4% was recorded for a sample dried over a weekend, suggesting that it might have contained a small amount of moisture. Therefore, a possible explanation for the observed behavior is that a small amount of NaVO\(_3\)·2H\(_2\)O in the undried samples provided the seed crystals for the precipitation of the dihydrate. However, kinetic issues are outside the scope of the present work and were not investigated further.

A few samples prepared from the undried NaVO\(_3\) were rotated in the apparatus at 298.15 K until all the solid had converted to the dihydrate. The solubility of NaVO\(_3\) after 44 and 50 days of equilibration was 1.116 mol/kg and 1.115 mol/kg, respectively (\( u(m) = 0.003 \) mol/kg). Two determinations (after 54 and 55 days) from another sample yielded values of 1.114 and 1.119 mol/kg, respectively, which are in a close agreement with the former results. However, if the solubility in the former sample is plotted as a function of 1/\( t \), a possible trend may be observed (Figure 1b). By linear extrapolation, the solubility of NaVO\(_3\) seems to approach a value of 1.101(3) mol/kg as \( t \rightarrow \infty \) (Figure 1b). Nevertheless, the experimentally observed values were only slightly larger than this value, and the reliability of the extrapolation cannot be assured. Therefore, we report the

### Table 2. Solubility of NaCl in Water at \( p = 0.101(1) \) MPa Measured in this Work and the Values Accepted in the Critical Review of Solubility Data Series\(^{32} \)

<table>
<thead>
<tr>
<th>T/K</th>
<th>this work ( m/(\text{mol/kg})^{b} )</th>
<th>IUPAC SDS ( m/(\text{mol/kg}) )</th>
<th>RD(^{\times 10^{3}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>6.139(4)</td>
<td>6.156(24)</td>
<td>-0.28</td>
</tr>
<tr>
<td>318.15</td>
<td>6.230(4)</td>
<td>6.248(24)</td>
<td>-0.29</td>
</tr>
<tr>
<td>328.15</td>
<td>6.305(4)</td>
<td>6.307(24)</td>
<td>-0.04</td>
</tr>
</tbody>
</table>

\(^{a}\)Standard uncertainty in \( T \) is \( u(T) = 0.01 \) K. \(^{b}\)Numbers in brackets correspond to one standard deviation in the last digits of each entry. \(^{c}\)Relative difference: \( \text{RD} = (m_{\text{this work}} - m_{\text{ref}})/m_{\text{ref}} \).

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**Figure 1.** (a) Molality of NaVO\(_3\) as a function of time at \( \sim 298.15 \) K for five different samples prepared from undried NaVO\(_3\) with varying liquid to solid ratios. (b) Molality as a function of \( r^{-1} \) in the sample with \( L/S = 25.8 \). Dots, experimental results; solid line, regression line; red dashed curves, the 95% confidence limits of the regression line.
The solubility of anhydrous NaVO$_3$ turned out to be especially difficult to measure. No reasonable results were obtained when the equilibrium was approached from supersaturation (decreasing $T$). The vanadium concentration declined only marginally when the temperature was lowered and could remain there for weeks. It seemed that kinetic factors hindered the precipitation of anhydrous NaVO$_3$, and we were forced to rely solely to replicated results obtained by approaching the equilibrium from undersaturation (increasing $T$). Erratic results were also obtained in temperatures below 328.15 K if the salt was not dried before preparing the sample. As mentioned above, the undried samples probably contained a small quantity of the dihydrate, which is metastable at least up to 323.15 K. Therefore, below 328.15 K, we accepted only results from samples in which the initial solid had been dried at 105 °C and stored in a desiccator before sample preparation. Considering these difficulties, it is no surprise that the reproducibility of the experimental results for NaVO$_3$ was the poorest of the three salts studied.

In the case of the NH$_4$VO$_3$·H$_2$O system, the points on the solubility curve were recorded by changing the temperature of the bath in the following order: 313.15 K → 298.15 K → 303.15 K → 328.15 K → 308.15 K → 318.15 K. This procedure enabled the direction of approach of the equilibrium to be varied. All the deviations from the regression curve were less than 0.5% indicating that the direction of approach had no effect on the results. Three or four days were sufficient for the NH$_4$VO$_3$·H$_2$O system to reach equilibrium. For example, the difference in the average molality of NH$_4$VO$_3$ measured in two samples after ca. 4 and 20 days of equilibration at 298.15 K was only $-3 \times 10^{-5}$ mol/kg, much less than the standard uncertainty of the measurement ($u = 2 \times 10^{-4}$ mol/kg).

The above observations illustrate well the experimental difficulties in studying the equilibrium properties of neutral aqueous V(V) systems. Due to the slow reactions, the possible simultaneous presence of at least two solid phases and the occurrence of metastable states it can be quite difficult to ensure the attainment of equilibrium in the NaVO$_3$·H$_2$O system. In contrast, the NH$_4$VO$_3$·H$_2$O system was found to be well behaved for the purposes of studying its equilibrium properties.

### Table 3. Experimental Solubilities of NaVO$_3$, NaVO$_3$·2H$_2$O, and NH$_4$VO$_3$ in H$_2$O Expressed as Molality $m$ at Temperature $T$ and $p = 0.101(1)$ MPa

<table>
<thead>
<tr>
<th>$T$/K</th>
<th>$m$/ (mol/kg)</th>
<th>$u$(m) × $10^5$</th>
<th>$m_{\text{meas}}$/ (mol/kg)</th>
<th>$R$/ RD</th>
<th>status</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaVO$_3$ (anhydrous)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298.15</td>
<td>1.530(7)</td>
<td>0.42</td>
<td>1.533</td>
<td>-0.18</td>
<td>A</td>
</tr>
<tr>
<td>303.15</td>
<td>1.662(28)</td>
<td>1.68</td>
<td>1.663</td>
<td>-0.08</td>
<td>A</td>
</tr>
<tr>
<td>308.15</td>
<td>1.835(23)</td>
<td>1.22</td>
<td>1.796</td>
<td>2.11</td>
<td>A</td>
</tr>
<tr>
<td>313.15</td>
<td>1.910(14)</td>
<td>0.70</td>
<td>1.931</td>
<td>-1.11</td>
<td>A</td>
</tr>
<tr>
<td>318.15</td>
<td>2.076(15)</td>
<td>0.70</td>
<td>2.067</td>
<td>0.43</td>
<td>A</td>
</tr>
<tr>
<td>323.15</td>
<td>2.206(65)</td>
<td>2.93</td>
<td>2.203</td>
<td>0.12</td>
<td>A</td>
</tr>
<tr>
<td>328.15</td>
<td>2.318(17)</td>
<td>0.71</td>
<td>2.339</td>
<td>-0.92</td>
<td>A</td>
</tr>
<tr>
<td>333.15</td>
<td>2.409(18)</td>
<td>0.71</td>
<td>2.474</td>
<td>0.63</td>
<td>A</td>
</tr>
<tr>
<td>NaVO$_3$·2H$_2$O (dihydrate)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298.15</td>
<td>1.116(3)</td>
<td>0.22</td>
<td>1.117</td>
<td>-0.08</td>
<td>A</td>
</tr>
<tr>
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<td>1.418(13)</td>
<td>0.87</td>
<td>1.403</td>
<td>1.04</td>
<td>A</td>
</tr>
<tr>
<td>308.15</td>
<td>1.816(10)</td>
<td>0.51</td>
<td>1.829</td>
<td>-0.74</td>
<td>A</td>
</tr>
<tr>
<td>313.15</td>
<td>2.419(18)</td>
<td>0.71</td>
<td>2.420</td>
<td>-0.03</td>
<td>A</td>
</tr>
<tr>
<td>318.15</td>
<td>3.202(23)</td>
<td>0.70</td>
<td>3.177</td>
<td>0.78</td>
<td>A</td>
</tr>
<tr>
<td>323.15</td>
<td>4.027(29)</td>
<td>0.72</td>
<td>4.043</td>
<td>-0.39</td>
<td>A</td>
</tr>
<tr>
<td>328.15</td>
<td>4.749</td>
<td>-</td>
<td>4.844</td>
<td>-1.99</td>
<td>T</td>
</tr>
<tr>
<td>333.15</td>
<td>5.049</td>
<td>-</td>
<td>5.285</td>
<td>-4.67</td>
<td>T</td>
</tr>
<tr>
<td>NH$_4$VO$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298.15</td>
<td>0.0594(2)</td>
<td>0.32</td>
<td>0.0594</td>
<td>0.01</td>
<td>A</td>
</tr>
<tr>
<td>303.15</td>
<td>0.0713(3)</td>
<td>0.31</td>
<td>0.0713</td>
<td>0.04</td>
<td>A</td>
</tr>
<tr>
<td>308.15</td>
<td>0.0853(4)</td>
<td>0.41</td>
<td>0.0855</td>
<td>-0.26</td>
<td>A</td>
</tr>
<tr>
<td>313.15</td>
<td>0.1026(10)</td>
<td>0.96</td>
<td>0.1023</td>
<td>0.46</td>
<td>A</td>
</tr>
<tr>
<td>318.15</td>
<td>0.1222(12)</td>
<td>0.97</td>
<td>0.1218</td>
<td>0.32</td>
<td>A</td>
</tr>
<tr>
<td>323.15</td>
<td>0.1433(25)</td>
<td>0.97</td>
<td>0.1439</td>
<td>-0.45</td>
<td>A</td>
</tr>
<tr>
<td>328.15</td>
<td>0.1685(17)</td>
<td>0.96</td>
<td>0.1685</td>
<td>-0.01</td>
<td>A</td>
</tr>
<tr>
<td>333.15</td>
<td>0.1953(19)</td>
<td>0.96</td>
<td>0.1951</td>
<td>0.09</td>
<td>A</td>
</tr>
</tbody>
</table>

$^a$Standard uncertainty in $T$ is $u(T) = 0.01$ K. $^b$Numbers in brackets are the combined standard uncertainties $u(m)$ in the last digits of each entry. $^{10}$The relative standard uncertainties $u(m)$ are given in the third column. Calculation details can be found in the SI. $^cRD = (m_{\text{meas}} - m_{\text{exp}})/m_{\text{exp}}$ calculated from the fit to the present data. $^d\text{Exp} = \text{accepted value}, \text{R} = \text{rejected value}, \text{T} = \text{tentative value.} \text{Precipitation of anhydrous NaVO}_3$ possible (see text).

Graphical comparison of the present values with the values in Table S4 is given in the SI in the form of deviation plots. The literature data for the system NaVO$_3$·H$_2$O have been plotted in Figure 2 along with the values measured in the present work. A total of 25 datapoints in 9 publications were found for the system NaVO$_3$·H$_2$O, $^{13,20,21,23,25,27,29,32}$ Only four papers, three of which come from the same group, $^{13,20,21}$ report solubilities for the anhydrous NaVO$_3$. The early results of McAdam and Pierle are in significant disagreement with the former. Only nine points in six rather dated publications were found for the solubility of NaVO$_3$·2H$_2$O.

The first three parameters $A_0$–$A_2$ of eq 1 were sufficient for correlating the solubility data for the anhydrous NaVO$_3$. In the case of NaVO$_3$·2H$_2$O and NH$_4$VO$_3$, the addition of a fourth parameter $A_3$ was required for an accurate representation of the data. The obtained regression parameters for the three salts
The solubilities of anhydrous NaVO₃ reported by McAdam and Pierle are about 10% higher than the other values. These authors used only glass wool to filter the solutions, so their samples may have contained colloidal particles. The authors also mentioned that the particles of anhydrous NaVO₃ were extremely small. Therefore, the results of McAdam and Pierle for the anhydrous salt were excluded from further analysis. The other results for anhydrous NaVO₃ in Tables 3 and S4 fall reasonably well on the regression line. The average relative deviation from the regression line is 0.33%, the largest negative and positive deviations being −2.50 and 3.81%, respectively. The residuals are about the same magnitude as the relative standard uncertainties, which vary between 0.42 and 2.93% with an average of 1.29%. The coefficient of determination calculated for the weighted least squares fit of Y versus T is $R^2_{WLS} = 0.9894$. Using only the values reported in the present work, a somewhat better fit is obtained (relative deviations: average: 0.13%, min: −1.11%, max: 2.11%, $R^2_{WLS} = 0.9975$).

The dihydrate solubilities reported in the literature are somewhat scattered but show fairly good overall agreement with our results. Most of the earlier values at 298.15 K are slightly higher than our estimate. A possible explanation for this discrepancy could lie in the extremely slow attainment of equilibrium, as discussed in Section 3.2. At least in two previous investigations the dihydrate was synthesized beforehand, whereas we prepared the dihydrate in-situ. If the NaVO₃·2H₂O used by the former workers contained traces of anhydrous NaVO₃, it might be that equilibrium had not yet been established in the few days of experiments of these workers. Discrepancies also arise in the values obtained at 333.15 K, which might result from the loss of metastability somewhere where we prepared the dihydrate and where the NaVO₃·2H₂O used in the experiments of these workers may have contained colloidal particles. The authors also used only glass wool to filter the solutions, so their samples may have contained colloidal particles. The results at 348.15 K the samples suddenly solidified. Therefore, the results above 323.15 K were excluded from the regression analysis and we recommend that results above this temperature are considered tentative at best. The data in the range 285.65–323.15 K were well described by eq 1 ($R^2_{WLS} = 0.9921$). The relative deviations of the accepted values from the regression line were 0.59% on average with a maximum of 8.80% and a minimum of −5.90%. The fit to the present data only was again better (relative deviations: average: 0.10%, min: −0.74%, max: 1.04%, $R^2_{WLS} = 0.9999$). It should be noted that the extrapolation of these curves beyond the experimentally covered temperature ranges is not justified.

Slightly different estimates are obtained for the temperature at the peritectic point depending on the data used in the regression. Using all the data for both solids, the regression lines intersect at

Table 4. Fitted Values of the Regression Parameters Appearing in Equation 1

<table>
<thead>
<tr>
<th>data used in the regression</th>
<th>$A_0$</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$A_3$</th>
<th>$R^2_{WLS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaVO₃ (tw)</td>
<td>21.4608</td>
<td>−27.3610</td>
<td>−17.8380</td>
<td>−</td>
<td>0.9975</td>
</tr>
<tr>
<td>NaVO₃ (all)</td>
<td>19.7860</td>
<td>−25.6492</td>
<td>−16.5527</td>
<td>−</td>
<td>0.9894</td>
</tr>
<tr>
<td>NaVO₃·2H₂O (tw)</td>
<td>−407.08788</td>
<td>5423.10203</td>
<td>10465.12605</td>
<td>−5019.82508</td>
<td>0.9999</td>
</tr>
<tr>
<td>NaVO₃·2H₂O (all)</td>
<td>−48.65218</td>
<td>473.29520</td>
<td>927.83953</td>
<td>−428.41612</td>
<td>0.9921</td>
</tr>
<tr>
<td>NH₄VO₃ (tw)</td>
<td>−52.6575</td>
<td>628.0764</td>
<td>1237.3946</td>
<td>−587.7171</td>
<td>1.0000</td>
</tr>
<tr>
<td>NH₄VO₃ (all)</td>
<td>13.8382</td>
<td>−77.3498</td>
<td>−105.6184</td>
<td>51.2358</td>
<td>0.9911</td>
</tr>
</tbody>
</table>

*Extra significant figures have been included to preserve numerical accuracy. *tw = Only data measured in this work, *all = Accepted data in Tables 3 and S4. *Calculated for weighted least squares fit $R^2_{WLS} = 1 - \sum (w_i (Y_i - \hat{Y}_i)^2) / \sum (w_i (Y_i - \bar{Y})^2)$. 

https://doi.org/10.1021/acs.jced.3c00367

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Figure 2. Solubility of NaVO₃ in water. Data marked with red color not used in the regression. Anhydrous NaVO₃: black squares, this work; blue circles, Mazurek and Druzynski; purple diamonds, Trypuć and Kielkowska; orange downward triangles, Trypuć and Druzynski; red upward triangles, McAdam and Pierle; solid line: Fit of eq 1 to all accepted data. Blue dash-dot line: Fit of eq 1 to the present data. NaVO₃·2H₂O: Filled circles, this work; plus signs, McAdam and Pierle; purple cross, Kiehl and Manfredo; blue asterisk, Ivakin et al.; dashed line: fit of eq 1 to all accepted data. Blue dotted line: fit of eq 1 to the present data.
307.5 K, whereas using only the present data, the point of intersection is located at 307.7 K.

The measured solubilities of NH₄VO₄ in water are given in Table 3 and have been plotted in Figure 3 along with the literature data in Table S4. The data obtained in the present work were extremely smooth, as all the relative deviations from the regression curve fitted to the data were less than 0.5% (relative deviations: average: 0.03%, min: −0.45%, max: 0.46%, R²_WLS = 1.0000). The fit to all the data in Tables 3 and S4 also represented the overall data well and was in good agreement with the present results (relative deviations: average: 0.24%, min: −22.05%, max: 13.74%, R²_WLS = 0.9911). In the low temperature end, the two regression curves coincide almost exactly but in higher temperatures, the present values are slightly lower than those estimated from the overall data. However, many of the literature datasets include points on both sides of the present regression curve. Especially the results of Trypuc and co-workers seem to be in good agreement with the present data as relative deviations from the fit to the present data do not exceed 5% apart from one exception.

3.4. Prediction of Solubility from Thermodynamic Considerations. The saturated solutions of NH₄VO₄ are sufficiently dilute that the reasonable estimation of activity coefficients by a simple expression could perhaps be possible. Therefore, it was thought worthwhile to examine how well the solubility of NH₄VO₄ could be predicted using only thermodynamic data available in the literature. In contrast, the modeling of activity coefficients in the more concentrated NaVO₄–H₂O systems can be expected to be much more complicated. Thus, we limit the present discussion to the NH₄VO₄–H₂O system.

The speciation of pentavalent vanadium in dilute ([V]_tot < 0.3 mol/kg) aqueous solutions has been the subject of a large number of studies, of which the most notable ones are the extensive investigations of Pettersson and co-workers. Some other studies worth mentioning include the studies by Larson, Tracey et al., and McCann et al. By coupling NMR measurements and potentiometric titrations, these investigators have determined the speciation in dilute V(V) solutions in various ionic media for a wide pH range. However, the apparent formation constants of many of the aqueous species have been found to depend strongly on the ionic strength and on the type and concentration of the cation of the background electrolyte. The latter observation suggests that ion pairs or complexes can form between some vanadate species and the cations in the solution. The equilibrium constants for most of the ion-pair/complex formation reactions remain unknown, and the number of possible species is so large that their determination can be expected to be challenging. To our knowledge, the only attempt to estimate such constants has been conducted by Pettersson some 20 years ago, who reported the formation constants at 298.15 K for a few sodium and tetrabutylammonium (TBA) complexes of mono- and divanadate species, covering a pH range of 10.8–12. Considering the above, the development of thermodynamic models capable of reproducing all the properties of even simple vanadate bearing systems, can be expected to be an extremely difficult if not overwhelming task. Here, we combine the speciation studies mentioned above with thermochemical data from the literature to investigate the capabilities of the current speciation models in predicting the solubility of NH₄VO₄ at 298.15 K.

The dissolution of NH₄VO₄ in water can be written as

\[
\text{NH}_4\text{VO}_4(s) + H_2O(l) \rightleftharpoons NH_4^+(aq) + H_2VO_4^-(aq)
\]  

(5)

The formation of the aqueous vanadate species can be described by the following general equation, in which \( p \) and \( q \) may get several integer values:

\[
pH^+(aq) + qHVO_4^{2-}(aq) \rightleftharpoons (H^+)_q(HVO_4^{2-})_q(aq)
\]  

(6)

The self-ionization of water and the deprotonation of the ammonium ion require two additional equilibrium relationships to be considered:

\[
H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)
\]  

(7)

\[
NH_4^+(aq) \rightleftharpoons NH_4(aq) + H^+(aq)
\]  

(8)

The equilibrium constants for reactions of type (6) were obtained from various speciation studies, whereas the equilibrium constants for reactions 5, 7, and 8 were calculated from tabulated Gibbs energy of formation data of the individual species (Table S6). It should be noted, that problems with internal consistency easily arise when \( \Delta G^0 \) values from different sources are combined. A particular example concerning the present case is the value of \( \Delta G^0(\text{H}_2\text{VO}_4^-,aq) \). Larson report a value of 1022.5 kJ/mol, whereas the 1982 NBS tables list values of 1020.8 and 1020.85 kJ/mol, respectively. A difference of 1.7 kJ/mol in the \( \Delta G^0 \) affects the log₁₀\( K \) value of eq 5 by 0.3 log-units. In fact, Larson’s value has been calculated combining an experimental equilibrium constant with the NBS 1982 value.

By coupling the JESS (Joint Expert Speciation System) software and database, the Gibbs energy changes assigned to individual

![Figure 3. Solubility of NH₄VO₄ in water. Black squares, this work; blue circles, Gong et al.; green diamonds, Yan et al.; red stars, Liu et al.; blue crosses, Meyer; blue rightward triangles, Andreev; yellow plus signs, Lachartre; orange downward triangles, Trypuc; brown hexagram, Gillard; solid line: fit of eq 1 to all data. Blue dashed line: fit of eq 1 to the present data.](https://doi.org/10.1021/acs.jced.3c00367)
species in the JESS database are not for the formation from elements, but for reactions involving a so-called basis set of species, which appear in reactions with the most reliable equilibrium constants. All the other species are represented by linear combinations of these basis reactions, which also conveniently ensures internal consistency. The database behind JESS is the world's largest collection of equilibrium constants and other thermodynamic properties. Of course, the estimates provided by JESS cannot be better than the data behind them, but the amount of data stored in the database and the requirement of internal consistency should ensure that the estimates are often reasonable. The ΔrG°(H₂VO₄⁻,aq) value obtained from JESS is 1021.8 kJ/mol, which lies almost in the middle of the two competing values. The utilization of JESS is almost certainly less risky than collecting single values from several literature sources. Therefore, the extra ΔrG° values required to extend the speciation models to cover solubility phenomena have been extracted from JESS using the online calculator tools provided by the developers.

The ΔrG° values calculated from ΔrG° are also susceptible to round-off errors. To avoid the propagation of errors in the literature, the best practice is to report equilibrium constants of the reactions (or ΔrG°) instead of ΔrG° values. However, it is often more practical to use the latter as inputs in computerized equilibrium calculations. The ΔrG° values used in the present calculations are reported with at least five significant figures in Table S6 and the equilibrium constants for the various reactions are listed in Table S5. To enable easy comparison with the literature, the values in Table S6 are reported for the conventional Gibbs energies of formation from the elements. Apart from those of Larson, all the equilibrium constants are based on concentrations rather than molalities, but the solutions have been so dilute that the difference between molality and molarity can be considered negligible.

The standard states for NH₄VO₃ (s) and H₂O (l) are the anhydrous salt and pure liquid water at 1 bar pressure, and that for the aqueous ions is the hypothetical 1 mol/kg solution obeying Henry's law. The Gibbs energy change for a reaction with all reactants and products in their standard states at any temperature T is given by

\[
\Delta_r G^0 = \Delta_r H^0_{298K} + \int_{298K}^T \Delta_r C_P^0 dT - T \left( \Delta_r S^0_{298K} + \int_{298K}^T \frac{\Delta_r C_P^0}{T} dT \right)
\]

where ΔrH°, ΔrS°, and ΔrC° are the standard enthalpy, entropy, and heat capacity changes of reaction. At 298.15 K, eq 9 reduces to ΔrG°(298K) = ΔrH°(298K) − TΔrS°(298K). On the other hand, ΔrG° can be expressed in terms of the equilibrium constant:

\[
\frac{-\Delta_r G^0}{RT} = \ln K = \prod_i \left( \gamma_i \frac{m_i}{v_i} \right)^{y_i} + v_w \ln a_w
\]

where γ, m, and v are the molal activity coefficient, equilibrium molarity, and the stoichiometric number of species i and a is the activity of water. An expression for the excess Gibbs energy of the system is needed to evaluate γ and a. This could be done by employing semi-empirical models of electrolyte solutions, such as the Pitzer equations. However, such models require empirically determined interaction parameters, which are not available for most of the species combinations appearing in the proposed speciation models. Thus, we approximate the activity coefficients of charged species with the simple Davies equation (eq 11) and set a_w = 1. Although the saturated solution of NH₄VO₃ is dilute, the accuracy of the Davies equation is questionable due to the presence of highly charged species such as V₄O₁₇⁺⁻ and to the possible existence of ion pairs/complexes between species.

\[
-\log_{10} K = 0.5085 z^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right)
\]

where z is the charge number of ion i and I = 0.5 ∑ z_i^2 m_i is the ionic strength of the solution.

The medium 0.05 M (TBA)Cl was thought to be somewhat similar to the saturated solution of NH₄VO₃ (e.g., with respect to I). If this was the case, the set of conditional equilibrium constants determined in such medium should yield an approximately correct estimate of solubility without a separate activity coefficient model. Likewise, the log10K values corresponding to infinite dilution coupled with some simple model for the activity coefficients could, in principle, be able to predict the NH₄VO₃ solubility correctly. To test these assumptions, the

### Table 5. Solubility of NH₄VO₃, pH, and Ionic Strength at 298.15 K Predicted by the Various Speciation Models

<table>
<thead>
<tr>
<th>Model</th>
<th>pH</th>
<th>pH</th>
<th>pH</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Larson⁸</td>
<td>65.5</td>
<td>6.71</td>
<td>0.0428</td>
<td></td>
</tr>
<tr>
<td>McCann et al.¹¹</td>
<td>72.6</td>
<td>5.44</td>
<td>0.0311</td>
<td></td>
</tr>
<tr>
<td>JESS⁷⁷</td>
<td>44.4</td>
<td>6.43</td>
<td>0.0493</td>
<td></td>
</tr>
<tr>
<td>Tracey et al.⁹</td>
<td>51.5</td>
<td>5.35</td>
<td>0.0660</td>
<td></td>
</tr>
<tr>
<td>Pettersson¹⁰</td>
<td>43.1</td>
<td>5.28</td>
<td>0.0802</td>
<td></td>
</tr>
</tbody>
</table>

**Table 5. Solubility of NH₄VO₃, pH, and Ionic Strength at 298.15 K Predicted by the Various Speciation Models**

- **Experimental solubility 0.0594(2) mol/kg.**
- **RD = (m_{exp} - m_{pred})/m_{exp}**

\[
\Delta_r G^0 = \Delta_r H^0_{298K} + \int_{298K}^T \Delta_r C_P^0 dT - T \left( \Delta_r S^0_{298K} + \int_{298K}^T \frac{\Delta_r C_P^0}{T} dT \right)
\]

\[
\frac{-\Delta_r G^0}{RT} = \ln K = \prod_i \left( \gamma_i \frac{m_i}{v_i} \right)^{y_i} + v_w \ln a_w
\]
sets of equilibrium constants given by the last five columns of Table S5 were applied with and without a simple activity coefficient model to make predictions of the solubility of NH\textsubscript{4}VO\textsubscript{3} at 298.15 K. The Δ\text{G}^\circ data given in Table S6 and stoichiometric matrices representing the reaction equations presented in this section were used as inputs in a self-written MATLAB routine which solved the equilibrium composition of the given system applying trust-region methods to solve the nonlinear minimization problem. The solubility, pH, and ionic strength predicted by each set of equilibrium constants is shown in Table 5. The equilibrium distribution of vanadium in the soluble species has been illustrated in Figure 4. The fraction of vanadium in each species was calculated as:

\[ \text{fraction of } m_{V,i} = \frac{q_i m_i}{\sum_{j=1}^{n} q_j m_j} \]  

(12)

where \( q_i \) is the number of vanadium atoms in the formula of species \( i \), \( m_i \) is the molality of that species, and the sum in the denominator is taken over all species in the solution.

The predicted solubilities of NH\textsubscript{4}VO\textsubscript{3} assuming unit activity coefficients are of correct magnitude, but clearly lower than the experimental value. If the activity coefficients are modeled with the Davies equation, the predicted solubility increases for all models and a somewhat better agreement is obtained. The models of Pettersson\textsuperscript{10} and Tracey\textsuperscript{9} now overestimate the solubility. Their equilibrium constants do not correspond to infinite dilution and already include the effects of nonideality to some extent, which could provide some explanation for this result. The predictions obtained using the data from Larson\textsuperscript{8} and from JESS\textsuperscript{8} are quite close to the experimental solubility with relative errors of 6.4 and \(-11.1\%\), whereas the model of McCann et al.\textsuperscript{11} still yields a low value.

All the models except the one based on the JESS database suggest that the dominant vanadium species in the saturated solution is the tetrameric anion V\textsubscript{4}O\textsubscript{12}\textsuperscript{4-}. The tetrameric species has indeed been identified as the dominant species in many solutions of similar composition by \textsuperscript{51}V NMR measurements.\textsuperscript{9,8,11,43} Most of the data for vanadium species in the JESS database has been given a low reliability rating and in many cases discrepant values of equilibrium constants for the same reaction are found in the database.\textsuperscript{8} For example, for the reaction given by eq 6 and \((p, q) = (2, 2)\), which corresponds to the formation of H\textsubscript{3}V\textsubscript{2}O\textsubscript{7}\textsuperscript{2-}, there are 4 entries with log\textsubscript{10}K values ranging from 18.1 to 21.1, determined in different ionic media. Consequently, it is not surprising that the calculated equilibrium composition differs from that calculated by the tailor-made speciation models. The differences in the proportions of the different species are a direct consequence of the discrepancies in the equilibrium constants extrapolated to infinite dilution. The three values for the formation constant of V\textsubscript{4}O\textsubscript{12}\textsuperscript{4-} by eq 6 in Table S5, which refer to infinite dilution vary by over 1 log-unit.

One possible explanation for the discrepancies is that the procedures used to extrapolate the results to infinite dilution have been deficient. It can be concluded that although the conditional formation constants in a few ionic media are known quite reliably, consensus is yet to be established for the values of the infinite dilution equilibrium constants.

Not much can be said about the correctness of these models based solely on the success or failure in predicting the solubility at a single temperature. All the above models have, however, a few obvious flaws that should be mentioned. First, the ion pairs or complexes between cations and the vanadate species have not been considered explicitly. It is important to note, that the charges of such complexes would be lower than those of the individual anions. This would naturally have a dramatic effect on the calculated ionic strength and on the activity coefficients of the involved species. A related issue is that the activity coefficients of highly charged ions are very sensitive to the ionic strength of the solution, and even small differences in the formation constants of such species have a substantial effect on the predicted ionic strength. Finally, uncertainties of even a few logarithmic units exist in the equilibrium constants extrapolated to infinite dilution. Despite the above issues, the predicted solubilities are of correct magnitude, and therefore, the formation of ion pairs/complexes do not necessarily need to be considered as distinct equilibria. It could perhaps be feasible to incorporate such effects into the parameters of an activity coefficient model. This possibility has been demonstrated by Pitzer and Mayorga for the case of 2\textsuperscript{+}−2\textsuperscript{−} electrolytes.\textsuperscript{62} More data covering a sufficiently large interval of ionic strength would be required to investigate this issue more closely.

In light of the above considerations, a thermodynamic model for aqueous V(V) systems should consider the polyoxovanadate species, which exist in appreciable concentrations in these solutions. Unfortunately, speciation studies have not been extended to concentrations corresponding to the saturated solutions of NaVO\textsubscript{3} and therefore, it remains uncertain which species dominate in such solutions. Moreover, the need to include ion pairs/complexes between vanadate species and medium cations in thermodynamic models for aqueous V(V) systems should be carefully assessed. The establishment of speciation in concentrated V(V) solutions could significantly advance the molecular level understanding of these systems. Also, more high-quality data on the macroscopic properties of V(V) solutions is needed to facilitate the development of semi-empirical models capable to reproduce the properties of these systems with sufficient accuracy for practical process modeling applications. Such data could include freezing point depression, isopiestic equilibration, and calorimetric measurements, for example.

4. CONCLUSIONS

The solubilities of NaVO\textsubscript{3}, NaVO\textsubscript{3}·2H\textsubscript{2}O and NH\textsubscript{4}VO\textsubscript{3} in water were measured using the isothermal saturation method and compared to previous solubility data available for these systems. Empirical equations correlating the solubility with temperature
were fitted to the data using the method of weighted least squares. The present data was consistent with the majority of previously published data and was also smoother, especially for the NH₄VO₃·H₂O system. Apparently for the first time, sufficient data points for the solubility of NaVO₂·2H₂O have been reported to allow the reliable tracing of the solubility curve for a considerable range of temperature. Several speciation models that have appeared in the literature were applied to predict the solubility of NH₄VO₃ at 298.15 K. The agreement of the predicted solubilities with the experimental data was approximate at best, although the models generally agreed on the identity of the major species in the solution. A few possible reasons for the limited predictive capabilities of these models were identified. For example, the identities and formation constants of the ion pairs/complexes that are likely to form between medium cations and some aqueous vanadate species remain mostly unknown. Moreover, there is currently no reliable method of weighted least squares. The present data was consistent with the majority of previously published data and was also smoother, especially for the NH₄VO₃·H₂O system. Apparently for the first time, sufficient data points for the solubility of NaVO₂·2H₂O have been reported to allow the reliable tracing of the solubility curve for a considerable range of temperature. Several speciation models that have appeared in the literature were applied to predict the solubility of NH₄VO₃ at 298.15 K. The agreement of the predicted solubilities with the experimental data was approximate at best, although the models generally agreed on the identity of the major species in the solution. A few possible reasons for the limited predictive capabilities of these models were identified. For example, the identities and formation constants of the ion pairs/complexes that are likely to form between medium cations and some aqueous vanadate species remain mostly unknown. Moreover, there is currently no reliable means to estimate activity coefficients in these systems. There is little point in attempting to construct temperature-dependent models for these systems before a reliable and consistent set of standard state thermodynamic properties at 298.15 K is established. Clearly, much work remains to be done if quantitatively accurate thermodynamic models even for the binary systems studied in the present work are to be realized.

**ASSOCIATED CONTENT**

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acs.jced.3c00367.

A detailed report on the estimation of uncertainty in this work; Tables S1—S3: Further details of experimental data and an example calculation of the standard uncertainty in solubility; Table S4: Literature data on the solubilities of NaVO₃, NaVO₂·2H₂O and NH₄VO₃ in H₂O; Table S5: Equilibrium constants for various reactions at 298.15 K determined in different ionic media; Figures S1—S3: Cause and effect diagrams illustrating the uncertainty sources; Figures S4 and S5: XRD patterns of the anhydrous NaVO₃ used as the starting material and of the residue remaining after the evaporative gravimetry; Figure S6: Results of the analyses of the "wet residue" of assumed NaVO₂·2H₂O phase and of its saturated solution; Figures S7—S9: Relative differences of experimental solubilities from those calculated by the correlation equations fitted to the present data; Figure S10: A photograph of the apparatus used in the solubility determinations (PDF).

Table S6: A table of standard Gibbs energies of formation at 298.15 K used in the thermodynamic calculations (XLSX).

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