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# Solubility Data for the $NaOH-NaNO_3-Na_3VO_4-Na_2CrO_4-H_2O$ System at (40 and 80) °C

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In a new vanadium production process, the effective separation of $Na_3VO_4$ and $Na_2CrO_4$ from the $NaOH-NaNO_3-Na_3VO_4-Na_2CrO_4-H_2O$ system plays a very important role. In this regard, the dissolution behavior of $Na_3VO_4$ and $Na_2CrO_4$ in the $NaOH-NaNO_3-Na_3VO_4-Na_2CrO_4-H_2O$ system was investigated by measuring solubility data, and finally the solubility diagram was constructed. From the data, a method of separating $Na_3VO_4$ via cooling crystallization and $Na_2CrO_4$ via evaporization in the concentrated alkaline solution is proposed.

## Introduction

Vanadium, as an important nonferrous metal, due to its stable chemical properties, such as resistance to oxidation in air, salt solution, acid, and alkali solutions,[1−4] is widely used in the iron and steel making industries. The consumption of vanadium in the iron and steel industries accounts for about 85 % of the total vanadium-bearing products worldwide.[5,6] Vanadium is usually processed using hydrometallurgical approaches, and the main operating units include roasting, leaching, solution purification, and vanadium precipitation.[7] Due to an advantage of simple process and easy operation, roasting of vanadium slag with sodium salts is currently the most popular vanadium extraction process,[8] but this process suffers from a low vanadium extraction efficiency and release of toxic gases such as HCl and $Cl_2$, causing serious environmental pollution.[9] The roasting process of vanadium slag with calcium salts solves the problem of toxic gas release, but the high-energy consumption and low vanadium extraction efficiency limit its application in industry.[10] Therefore, it is necessary to develop a highly efficient and environmentally friendly vanadium extraction process which excels in both vanadium recovery and operational easiness. Recently, such a process for vanadium production was developed by the Institute of Process Engineering, Chinese Academy of Sciences,[11] and compared to the traditional processes. The new technology shortens the reaction time, greatly increases the vanadium recovery efficiency, and more importantly is environmentally friendly. In this new vanadium extraction process, vanadium slag was first treated with a $NaOH-NaNO_3$ molten salt at 400 °C, with oxygen as oxidant, followed by dissolution with water. The solution obtained is a mixture of NaOH, $NaNO_3$, $Na_3VO_4$, and $Na_2CrO_4$ at 80 °C. A typical concentration of the solution obtained is as follows: NaOH (200 to 250) $g \cdot L^{-1}$, $NaNO_3$ (200 to 250) $g \cdot L^{-1}$, $Na_3VO_4$ (50 to 70) $g \cdot L^{-1}$ and $Na_2CrO_4$ (40 to 60) $g \cdot L^{-1}$. However, the concentration of the solution is not constant, as it can change based on the ratio of NaOH to $NaNO_3$ added at the reaction phase and the amount of dissolution water. Therefore, the effective separation of $Na_2CrO_4$ and $Na_3VO_4$ is critical in this process. From some solubility data of $NaOH-NaNO_3-H_2O$ [(20 and 70) °C], $NaOH-Na_3VO_4-H_2O$ [(40 and 80) °C], and $NaOH-Na_2CrO_4-H_2O$ [(40 and 80) °C],[12−15] it is proposed that $Na_2CrO_4$, $NaNO_3$, and $Na_3VO_4$ can be separated via crystallization based on their dissolution behavior in alkaline solutions at different temperatures. The preliminary experiments based on the solution obtained after reaction indicated that crystallization is indeed an effective way to achieve the multicomponent separation from the alkaline solution. The present study on the phase equilibrium of $NaOH-NaNO_3-H_2O$ and $NaOH-Na_3VO_4-H_2O$ was focused on a low alkaline concentration but cannot satisfy the separation of $NaNO_3$ and $Na_3VO_4$ at the high NaOH concentration in our reaearch. A study of the phase equilibrium of the $NaOH-Na_2CrO_4-H_2O$ system was appropriate to our research. The solubility data of the $NaOH-NaNO_3-Na_3VO_4-Na_2CrO_4-H_2O$ and $NaOH-NaNO_3-Na_3VO_4-H_2O$ systems have not been studied yet. Due to the lack of the above data, the design of an industrially applicable effective separation strategy is not yet able to be accomplished. In this regard, the solubility data of the $NaOH-NaNO_3-Na_3VO_4-Na_2CrO_4-H_2O$ system and its subsystems including $NaOH-NaNO_3-H_2O$, $NaOH-Na_3VO_4-H_2O$, and $NaOH-NaNO_3-Na_3VO_4-H_2O$ at (80 and 40) °C were studied in detail. On the basis of the findings, a proper crystallization strategy is proposed to effectively separate $Na_2CrO_4$, $NaNO_3$, and $Na_3VO_4$ from alkaline solutions.

## Experimental Section

***Apparatus and Reagents.*** An HZ-9212S type thermostatted shaking water bath with a precision of ± 0.1 °C was used for preparing samples at 40 °C. A specially designed HZ-9612K thermostatted shaking air bath with a precision of ± 0.2 °C was used for preparing samples at 80 °C. All chemicals used in this work, including NaOH, $NaNO_3$, $Na_2CrO_4 \cdot 4H_2O$, and $Na_3VO_4 \cdot 12H_2O$, were of analytical grade and manufactured by

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**Table 1. Solubility Data for the $NaOH-Na_3VO_4-H_2O$ System**

| composition of the liquid phase ($g{\cdot}L^{-1}$) | | | |
|---|---|---|---|
| $T$ = 40 °C | | $T$ = 80 °C | |
| NaOH | $Na_3VO_4$ | NaOH | $Na_3VO_4$ |
| 151.22 | 150.41 | 105.19 | 268.57 |
| 249.83 | 51.38 | 248.33 | 164.29 |
| 296.79 | 28.92 | 388.95 | 114.01 |
| 305.02 | 26.17 | 409.76 | 102.16 |
| 329.83 | 17.06 | 440.21 | 92.62 |
| 373.56 | 17.60 | 528.25 | 90.02 |
| 382.71 | 13.71 | 547.60 | 86.62 |
| 402.68 | 9.89 | 578.28 | 88.78 |
| 435.66 | 10.78 | 582.54 | 85.71 |
| 479.67 | 8.33 | 607.07 | 87.16 |
| 534.26 | 7.99 | 620.43 | 84.81 |
| 535.23 | 8.51 | | |
| 541.39 | 10.19 | | |
| 620.43 | 17.12 | | |
| 666.35 | 28.79 | | |

the Beijing Reagents Company. High-purity Milli-Q water, with a resistivity of above 18.2 MΩ·cm at ambient temperature, was used.

***Procedure.*** The supersaturated solutions were prepared by two methods. One was dissolving $Na_2CrO_4$, $NaNO_3$, and $Na_3VO_4$ in hot NaOH solutions. First, an alkaline solution was prepared by dissolving a certain amount of NaOH in high purity water in a flask positioned in a constant-temperature controlled water bath with the temperature fluctuation of less than ± 0.1 °C. Then the salts were added to the alkaline solutions while stirring, and the stirring was stopped when the salts did not dissolve any more. These supersaturated solutions were then transferred into sealed polyethylene bottles, which were placed in theromstatted shaking baths maintained at temperatures of (40 ± 0.1) °C and (80 ± 0.2) °C. The other is the addition of different solid phases at constant temperature [(40 and 80) °C] until they cannot be dissolved. Sampling of the liquid phase was performed every week to determine whether the equilibrium state was reached, and an equilibrium state is supposed to be achieved when the composition of the liquid phase did not change with time. If the liquid phase of the samples prepared by the two methods had the same trend, we could affirm that our samples were in the equilibrium state. Once the system was in the equilibrium state, the shaking was stopped, and the samples were kept in the baths for two more days for the suspended crystals to sediment. Next, the liquid phase of the samples were taken using a sampling gun, and to prevent the crystallization of the salts on the sampling tube surfaces, the sampling tubes were first heated to the predetermined temperatures. For each sampling, 1 mL of solution was taken and placed into a volumetric flask, followed by dilution with high-purity water for further analysis. The contents of $Na_2CrO_4$ and $Na_3VO_4$ in all samples were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, Perkin-Elmer, Optima 5300DV). The $NaNO_3$ content was determined by Ion Chromatography (Dionex, DX-500) and NaOH by titration using phenolphthalein as an indicator and titrated by dilute hydrochloric acid. For each system, three parallel samples were taken and measured, and the average of the three measurements was reported.

## Results and Discussion

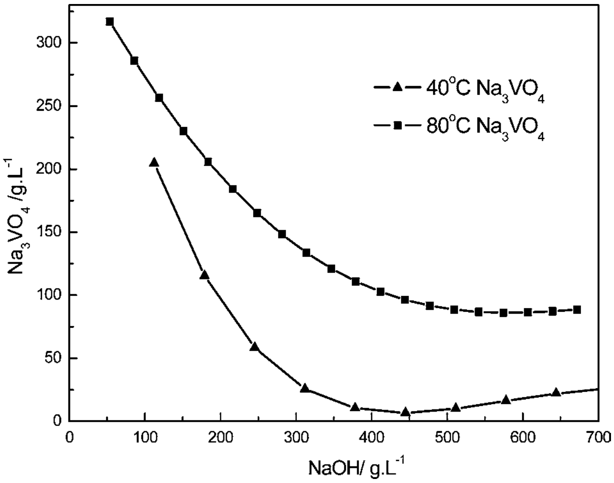

**Figure 1.** Solubility diagram of the $NaOH-Na_3VO_4-H_2O$ system.

**Table 2. Solubility Data for the $NaOH-NaNO_3-H_2O$ System**

| composition of the liquid phase ($g{\cdot}L^{-1}$) | | | |
|---|---|---|---|
| $T$ = 40 °C | | $T$ = 80 °C | |
| NaOH | $NaNO_3$ | NaOH | $NaNO_3$ |
| 0 | 664.30 | 0 | 926.09 |
| 57.95 | 609.19 | 125.10 | 734.18 |
| 127.49 | 494.97 | 275.22 | 529.06 |
| 150.67 | 440.97 | 325.26 | 512.19 |
| 266.57 | 331.36 | 375.30 | 449.68 |
| 312.93 | 261.38 | 450.36 | 376.60 |
| 370.88 | 201.94 | 500.40 | 392.51 |
| 428.83 | 164.65 | 550.44 | 349.60 |
| 452.01 | 163.62 | 575.46 | 344.66 |
| 498.37 | 131.75 | 650.52 | 344.11 |
| 567.91 | 120.92 | 675.54 | 341.37 |
| 591.09 | 125.79 | 725.58 | 322.45 |
| 683.81 | 123.80 | | |

***$NaOH-Na_3VO_4-H_2O$ System.*** The equilibrium data for the $NaOH-Na_3VO_4-H_2O$ system are presented in Table 1. Figure 1 shows the solubility diagram of this system. As can be seen in Figure 1, in the low-alkali region (that is, the region where the NaOH concentration < 300 $g{\cdot}L^{-1}$), there is an obvious decrease in the solubility of $Na_3VO_4$ with an increase of the NaOH concentration. So, it is possible to separate $Na_3VO_4$ in this region using evaporative crystallization. However, when the NaOH concentration is above 300 $g{\cdot}L^{-1}$, the concentration of $Na_3VO_4$ does not show any more significant change with an increase of NaOH concentration, excluding the possibility of separating $Na_3VO_4$ via evaporative crystallization. On the other hand, within the whole NaOH concentration range, there is an obvious difference in the solubility of $Na_3VO_4$ with temperature. So cooling crystallization could be an excellent method to extract $Na_3VO_4$ too. However, which method is better depends on the specific process.

***$NaOH-NaNO_3-H_2O$ System.*** The equilibrium data for the $NaOH-NaNO_3-H_2O$ system are presented in Table 2. Figure 2 shows the solubility diagram of this system. It is clear from Figure 2 that the solubility of $NaNO_3$ decreases sharply with an increase in the NaOH concentration until the concentration reaches 500 $g{\cdot}L^{-1}$. Therefore, it is expected that $NaNO_3$ can be extracted using vaporization crystallization. In addition, due to the appreciable temperature dependence of $NaNO_3$ solubility, cooling of the solution from (80 to 40) °C will also be effective to crystallize $NaNO_3$. Further, from Figure 2, neither evaporative crystallization nor cooling crystallization is capable of extracting $NaNO_3$ out of the alkaline solution completely. To maximize the crystallization efficiency of $NaNO_3$, it is advisible to integrate both methods. For example, when the NaOH concentration is 50 $g{\cdot}L^{-1}$, the largest theoretical crystallization efficiency via cooling is 27.6 % and via evaporation at (80 and 40) °C to 500 $g{\cdot}L^{-1}$ alkaline solution is 60.9 % (40 °C) and 80.2 % (80 °C),

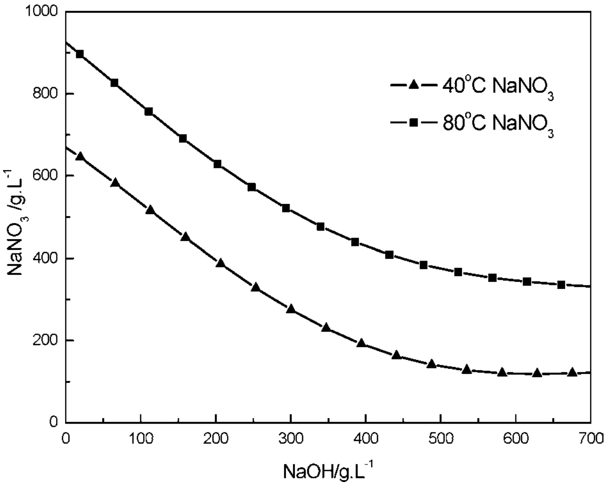

**Figure 2.** Solubility diagram of the NaOH−NaNO$_3$−H$_2$O system.

**Table 3. Solubility Data for the NaOH−NaNO$_3$−Na$_3$VO$_4$−H$_2$O System**

| composition of the liquid phase (g·L$^{-1}$) | | | | | |
|---|---|---|---|---|---|
| $T$ = 40 °C | | | $T$ = 80 °C | | |
| NaOH | NaNO$_3$ | Na$_3$VO$_4$ | NaOH | NaNO$_3$ | Na$_3$VO$_4$ |
| 0 | 586.77 | 206.12 | 167.57 | 760.28 | 99.87 |
| 69.98 | 563.47 | 31.74 | 181.47 | 700.77 | 95.05 |
| 118.96 | 492.86 | 19.63 | 271.69 | 598.46 | 49.32 |
| 188.77 | 466.81 | 22.44 | 292.24 | 556.61 | 53.18 |
| 322.65 | 318.06 | 11.04 | 338.28 | 505.54 | 47.05 |
| 325.75 | 291.33 | 6.95 | 410.56 | 451.73 | 60.96 |
| 389.96 | 270.08 | 10.47 | 473.34 | 400.02 | 54.25 |
| 458.60 | 230.32 | 7.58 | 478.22 | 387.30 | 50.60 |
| 465.86 | 233.75 | 10.21 | 617.30 | 355.60 | 32.84 |
| 526.38 | 224.84 | 10.47 | 661.19 | 348.91 | 46.65 |
| 602.08 | 207.02 | 18.26 | | | |
| 649.40 | 199.48 | 27.13 | | | |
| 568.96 | 196.05 | 26.69 | | | |
| 709.06 | 199.48 | 21.66 | | | |

respectively. However, if the solution is evaporated from NaOH concentration of 50 g·L$^{-1}$ to the NaOH concentration of above 500 g·L$^{-1}$ at 80 °C, followed by cooling to 40 °C, the crystallization efficiency could reach 85.6 %, which is higher than the two above-mentioned methods. In summary, NaNO$_3$ can be crystallized using cooling crystallization, evaporative crystallization, and the dynamic integration of the two methods, and the choice of the actual strategy is dependent on the industrial operation.

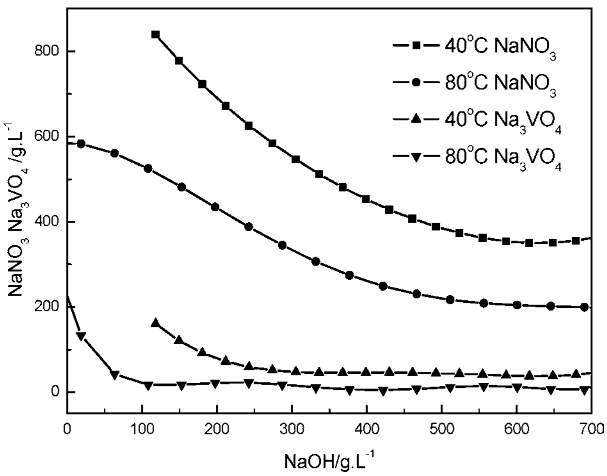

**Figure 3.** Solubility diagram of the NaOH−NaNO$_3$−Na$_3$VO$_4$−H$_2$O system.

***NaOH−NaNO$_3$−Na$_3$VO$_4$−H$_2$O System.*** The equilibrium data for the NaOH−NaNO$_3$−Na$_3$VO$_4$−H$_2$O system are presented in Table 3. Figure 3 shows the solubility diagram of this system. The salting out effect between Na$_3$VO$_4$ and NaNO$_3$ can be studied well by comparison of their solubility in the ternary systems (Figure 1 and Figure 2) and the quaternary system as presented in Figure 3. It is obvious that with the addition of NaNO$_3$ there is no significant change in the trend of Na$_3$VO$_4$ solubility with alkali concentration, but clearly the solubility of Na$_3$VO$_4$ decreases. So NaNO$_3$ has a salting out impact on Na$_3$VO$_4$. Similarly, Na$_3$VO$_4$ has a salting out impact on NaNO$_3$ too.

***NaOH−NaNO$_3$−Na$_3$VO$_4$−Na$_2$CrO$_4$−H$_2$O System.*** Equilibrium data for the NaOH−NaNO$_3$−Na$_3$VO$_4$−Na$_2$CrO$_4$−H$_2$O system are presented in Table 4. Figure 4 shows the solubility diagram of this system at (40 and 80) °C, respectively. Figure 4 shows that with the addition of Na$_2$CrO$_4$ into the system there is no obvious change to Na$_3$VO$_4$ solubility. However, in terms of NaNO$_3$, the salting out impact of Na$_2$CrO$_4$ on NaNO$_3$ is obvious, especially in low-alkali solution. In this region, to maximize the purity of Na$_3$VO$_4$, it is advisible to keep the NaNO$_3$ solubility under 200 g·L$^{-1}$. Figure 4 shows that the solubility of Na$_2$CrO$_4$ does not show significant dependence on temperature, so cooling will not be effective to crystallize Na$_2$CrO$_4$. On the other hand, the Na$_2$CrO$_4$ solubility is strongly dependent on the NaOH concentration, so evaporative crystal-

**Table 4. Solubility Data for the NaOH−NaNO$_3$−Na$_3$VO$_4$−Na$_2$CrO$_4$−H$_2$O System**

| composition of the liquid phase (g·L$^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|
| $T$ = 40 °C | | | | $T$ = 80 °C | | | |
| NaOH | NaNO$_3$ | Na$_3$VO$_4$ | Na$_2$CrO$_4$ | NaOH | NaNO$_3$ | Na$_3$VO$_4$ | Na$_2$CrO$_4$ |
| 0 | 332.43 | 192.48 | | 129.02 | 378.18 | 89.08 | 435.16 |
| 110.67 | 232.23 | 23.52 | 442.38 | 133.18 | | 69.92 | 423.22 |
| 170.55 | 236.70 | 14.29 | | 162.62 | 363.31 | 64.91 | 411.67 |
| 220.08 | 175.28 | 8.37 | 347.05 | 250.82 | 330.22 | 50.69 | 335.53 |
| 288.11 | 161.09 | 6.13 | 305.46 | 260.69 | 332.61 | 45.46 | |
| 336.54 | 152.38 | 5.23 | 279.64 | 379.50 | 304.77 | 51.01 | 222.35 |
| 365.49 | 149.64 | 5.20 | | 466.12 | | 54.19 | 182.19 |
| 419.00 | 138.47 | 5.74 | 215.30 | 502.81 | 285.71 | 55.85 | 151.44 |
| 499.63 | 126.27 | 9.52 | 146.83 | 639.83 | 266.58 | 47.94 | 116.89 |
| 528.18 | 125.51 | 11.29 | 132.78 | 695.23 | 63.31 | 54.01 | 112.62 |
| 581.14 | 127.29 | 13.98 | 94.96 | 772.45 | 267.69 | 42.37 | 104.68 |
| 666.37 | 123.04 | 14.34 | 72.74 | 779.57 | | 47.54 | 108.66 |
| 671.23 | 126.74 | 15.98 | 82.18 | 798.30 | 265.71 | 41.54 | 106.92 |
| 705.35 | 128.39 | 14.54 | 71.87 | | | | |
| 718.38 | 134.83 | 13.99 | 71.86 | | | | |
| 788.07 | 135.00 | 14.14 | 71.21 | | | | |

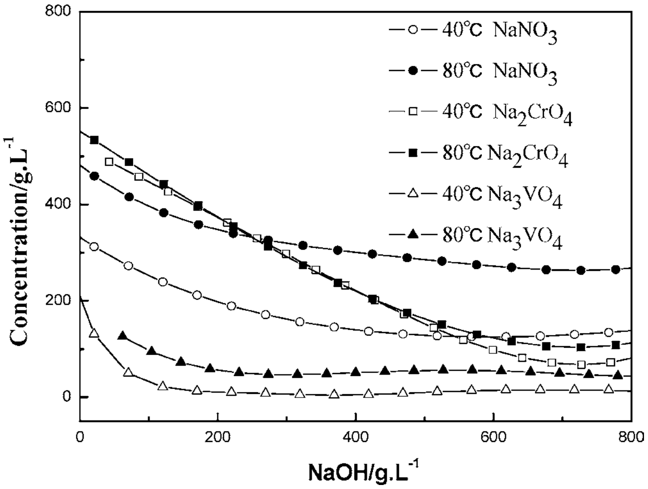

**Figure 4.** Solubility diagram of the $NaOH-NaNO_3-Na_3VO_4-Na_2CrO_4-H_2O$ system.

lization appears to be an effective way to crystallize $Na_2CrO_4$. Further, to maximize the yield of $Na_2CrO_4$, the alkaline solution is suggested to be evaporated to a NaOH concentration of above 500 $g \cdot L^{-1}$.

## Conclusions

Solubility data of the $NaOH-NaNO_3-Na_3VO_4-Na_2CrO_4-H_2O$ system and some of its subsystems at (40 and 80) °C were studied. From the data obtained from the experiment, a method of separating $Na_3VO_4$ via cooling crystallization, $NaNO_3$ via evaporative and cooling crystallization, and $Na_2CrO_4$ via evaporative crystallization in the new process is proposed.

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