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# Articles

## Solubility Investigations in the NaCl + $V_2O_5$ + $H_2O$ System from 293 K to 323 K

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The mutual solubility of NaCl and $V_2O_5$ in water in the temperature range 293−323 K is reported. The results are used to plot part of the polythermal solubility surface for the system NaCl + $V_2O_5$ + $H_2O$. The data are useful in the determination of the optimum operating parameters for production of sodium metavanadate by reacting NaCl and $V_2O_5$ in the presence of either steam or oxygen.

### Introduction

Sodium carbonate is generated from $NaVO_3$, which is synthesized from NaCl and $V_2O_5$ in the presence of steam or oxygen according to the following equations:

$$2NaCl + V_2O_5 + H_2O \rightarrow 2NaVO_3 + 2HCl \qquad (1)$$

$$4NaCl + 2V_2O_5 + O_2 \rightarrow 4NaVO_3 + 2Cl_2 \qquad (2)$$

The reaction can be carried out without causing serious environmental concerns.[1−3]

The sodium metavanadate is an intermediate reactant which is subsequently transformed by several unit processes into the final product sodium carbonate (similar to the case of the Solvay method).[4,5]

Undertaken investigations on the $NaVO_3$ synthesis, expressed by reactions 1 and 2, indicate clearly that the conversion degree of $V_2O_5$ into $NaVO_3$ is strictly correlated with temperature, time of processing, amount of NaCl, steam, or oxygen present in the reaction mixture, and granulation degree of the reagents, that is, $V_2O_5$ and NaCl.[1,2,6]

The maximum possible degree of $V_2O_5$ conversion of about 95% is achieved in a constructed flow reactor at $T$ = 823 K, with a 4 h time of processing with 20% NaCl excess and 10 times steam excess. According to literature data, the $V_2O_5$ conversion degree is estimated at 90% ($T$ = 823 K, 10% NaCl excess in the reaction mixture).[1]

The maximum reaction yield of 66.54 for reaction 2 was achieved with an 8 h duration with reagent amounts maintained at their stoichiometric ratios. Further investigations on optimization of the operating parameters will be carried out.[7]

To determine the optimum operating conditions for the $NaVO_3$ separation procedure out of the postreaction mixture, a detailed knowledge of the mutual solubility of NaCl, $V_2O_5$, and $NaVO_3$ in water is essential. Data for the following systems have been studied:

**Table 1. Comparison of Solubility Data Presented in This Work with the Literature Data for the Binary System NaCl + $H_2O$**

| | $m$/(mol·kg$^{-1}$ of $H_2O$) | | | |
|---|---|---|---|---|
| ref | 293 K | 303 K | 313 K | 323 K |
| this work | 6.147 | 6.195 | 6.251 | 6.294 |
| Cohen-Adad and Lorimer[8] | 6.140 | 6.174 | 6.223 | 6.277 |
| Sytniewski[9,10] | 6.140 | 6.178 | 6.224 | 6.279 |

$$NaCl + V_2O_5 + H_2O$$

$$NaVO_3 + V_2O_5 + H_2O$$

$$NaCl + NaVO_3 + V_2O_5 + H_2O$$

This paper deals with the mutual solubility of components, which enables the determination of the series of isothermal sections of the phase diagram for the system NaCl + $V_2O_5$ + $H_2O$ in the temperature range 293−323 K.

No solubility data have been found in the profound literature review concerning the title system.

A compilation of the solubility data for the binary system NaCl + $H_2O$ has been done recently, and modeling of liquid curves has been performed.[8−10]

### Experimental Part

***Chemicals.*** Analytical purity grade chemicals were used for all of the experiments: NaCl (99.9% POCH S.A. Poland), $V_2O_5$ (98%, Aldrich Chemical Co., Inc.).

***Experimental Procedure.*** The mutual solubility investigations in the NaCl + $V_2O_5$ + $H_2O$ system were carried out at 293, 303, 313, and 323 K, employing the isothermal solution saturation technique.

Erlenmeyer flasks, each of 100 cm$^3$ capacity, containing the projected amount of components and water were placed in a thermostated bath until the equilibrium between the solid phase and solution was achieved. All samples were continuously stirred using magnetic stirrers. A Polystat

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**Table 2. Experimental Results for the Mutual Solubility of Sodium Chloride and Vanadium (V) Oxide in Water**

|  | $c/(\mathrm{mol \cdot dm^{-3}})$ | $10^4 c/(\mathrm{mol \cdot dm^{-3}})$ |  |  | $c/(\mathrm{mol \cdot dm^{-3}})$ | $10^4 c/(\mathrm{mol \cdot dm^{-3}})$ |  |
|---|---|---|---|---|---|---|---|
| $\rho/(\mathrm{g \cdot cm^{-3}})$ | NaCl | $V_2O_5$ | solid phase | $\rho/(\mathrm{g \cdot cm^{-3}})$ | NaCl | $V_2O_5$ | solid phase |
|  | $T = 293$ K |  |  |  | $T = 303$ K |  |  |
| 1.197 | 5.413 | 0 | NaCl | 1.193 | 5.426 | 0.000 | NaCl |
| 1.197 | 5.441 | 1.071 | NaCl | 1.194 | 5.438 | 0.456 | NaCl |
| 1.198 | 5.451 | 1.769 | NaCl | 1.194 | 5.448 | 1.082 | NaCl |
| 1.198 | 5.458 | 2.630 | NaCl | 1.195 | 5.457 | 2.016 | NaCl |
| 1.198 | 5.458 | 3.110 | NaCl | 1.195 | 5.464 | 3.210 | NaCl |
| 1.199 | 5.459 | 3.400 | NaCl | 1.195 | 5.464 | 3.981 | NaCl |
| 1.199 | 5.459 | 4.092 | NaCl | 1.195 | 5.463 | 4.807 | NaCl |
| 1.199 | 5.458 | 4.913 | NaCl | 1.196 | 5.463 | 5.280 | NaCl |
| 1.199 | 5.458 | 5.863 | NaCl | 1.196 | 5.463 | 5.939 | NaCl, $V_2O_5$ |
| 1.199 | 5.458 | 6.385 | NaCl, $V_2O_5$ | 1.189 | 4.818 | 5.940 | $V_2O_5$ |
| 1.176 | 4.792 | 6.598 | $V_2O_5$ | 1.161 | 3.940 | 6.350 | $V_2O_5$ |
| 1.150 | 4.206 | 6.920 | $V_2O_5$ | 1.124 | 3.305 | 6.840 | $V_2O_5$ |
| 1.127 | 3.180 | 7.930 | $V_2O_5$ | 1.090 | 2.467 | 8.021 | $V_2O_5$ |
| 1.096 | 2.081 | 9.680 | $V_2O_5$ | 1.066 | 1.910 | 9.000 | $V_2O_5$ |
| 1.058 | 1.250 | 11.67 | $V_2O_5$ | 1.035 | 1.320 | 10.41 | $V_2O_5$ |
| 1.027 | 0.782 | 13.51 | $V_2O_5$ | 1.007 | 0.400 | 14.53 | $V_2O_5$ |
| 1.015 | 0.310 | 15.19 | $V_2O_5$ | 0.999 | 0.930 | 18.42 | $V_2O_5$ |
| 0.997 | 0 | 20.46 | $V_2O_5$ | 0.998 | 0 | 21.60 | $V_2O_5$ |
|  | $T = 313$ K |  |  |  | $T = 323$ K |  |  |
| 1.188 | 5.439 | 0 | NaCl | 1.184 | 5.448 | 0 | NaCl |
| 1.190 | 5.440 | 0.074 | NaCl | 1.186 | 5.454 | 0.310 | NaCl |
| 1.191 | 5.445 | 0.229 | NaCl | 1.187 | 5.461 | 0.620 | NaCl |
| 1.192 | 5.453 | 0.690 | NaCl | 1.188 | 5.465 | 1.020 | NaCl |
| 1.192 | 5.459 | 1.121 | NaCl | 1.188 | 5.469 | 1.420 | NaCl |
| 1.192 | 5.463 | 1.650 | NaCl | 1.189 | 5.470 | 1.698 | NaCl |
| 1.192 | 5.466 | 1.834 | NaCl | 1.190 | 5.474 | 2.560 | NaCl |
| 1.193 | 5.468 | 2.650 | NaCl | 1.190 | 5.476 | 3.070 | NaCl |
| 1.193 | 5.469 | 3.836 | NaCl | 1.190 | 5.477 | 3.699 | NaCl |
| 1.193 | 5.468 | 4.900 | NaCl | 1.190 | 5.475 | 4.401 | NaCl |
| 1.193 | 5.468 | 4.493 | NaCl | 1.191 | 5.476 | 4.992 | NaCl |
| 1.193 | 5.467 | 5.605 | NaCl, $V_2O_5$ | 1.191 | 5.475 | 5.191 | NaCl, $V_2O_5$ |
| 1.155 | 5.030 | 5.670 | $V_2O_5$ | 1.172 | 4.811 | 5.200 | $V_2O_5$ |
| 1.154 | 4.283 | 5.820 | $V_2O_5$ | 1.155 | 4.091 | 5.270 | $V_2O_5$ |
| 1.110 | 3.034 | 6.151 | $V_2O_5$ | 1.108 | 3.156 | 5.650 | $V_2O_5$ |
| 1.075 | 2.390 | 7.310 | $V_2O_5$ | 1.061 | 2.220 | 7.091 | $V_2O_5$ |
| 1.040 | 1.691 | 8.751 | $V_2O_5$ | 1.038 | 1.403 | 8.880 | $V_2O_5$ |
| 1.021 | 0.800 | 11.42 | $V_2O_5$ | 1.024 | 0.806 | 10.95 | $V_2O_5$ |
| 1.012 | 0.319 | 15.10 | $V_2O_5$ | 1.001 | 0.335 | 13.51 | $V_2O_5$ |
| 1.000 | 0.176 | 18.43 | $V_2O_5$ | 1.000 | 0.124 | 17.00 | $V_2O_5$ |
| 0.999 | 0 | 21.85 | $V_2O_5$ | 0.999 | 0 | 22.20 | $V_2O_5$ |

CC1 thermorelay (Germany), with a precision of ±0.02 K was used for the experimental equilibrium.

The experimental time of thermostating was 120 h.

After a fixed time interval, stirring was discontinued and solids were sedimented.

The clear equilibrium solution was transferred into a Ostwald pycnometer calibrated at a given temperature . The total pycnometer content was employed for the solution density determination.

The uncertainty of density measurements was estimated to be $\pm 0.002\ \mathrm{g \cdot cm^{-3}}$.

Then the solution was transferred quantitatively to the graduated flask and diluted using distilled water, and the chloride ion and vanadium concentration measurements were performed.

***Analytical Methods.*** The chloride ion concentration was evaluated using the potentiometric titration method (716 DMS Titrino titrator, Switzerland) with a combined silver electrode.[11- 13]

A diluted solution of $H_2SO_4$ acid (1:9) was introduced into each sample; next each sample was titrated using a 0.1 M solution of $AgNO_3$.

Obviously, the presence of vanadium(V) implies a very low repeatability of the end point of titration for low concentrations of $Cl^-$ ions. Therefore, vanadium(V) was reduced using the solution of sodium sulfite in diluted (1:7) sulfuric acid.[12] In all reduced samples, the concentration of chloride ions was evaluated by means of the argentometric method analogous to that employed in solutions without preliminary reduction. The average relative error of the measurements was estimated to be ±0.5%.

The concentration of vanadium(V) was determined using the spectrophotometric method with a double beam UV/VIS U-2000 (HITACHI) spectrophotometer. The formation effect of colored complexes by vanadium ions with 4-(2-pyridyloazo)resorcinol (PAR)[12,14] was employed. This agent is known for its reactivity with vanadium compounds. The optimum pH for the complex stability is determined to be within 5−6 with the maximum absorbency at $\lambda = 543$ nm. The sodium salt of PAR was used because of its fair solubility in water. The determination accuracy was ±2%.

***Identification of Solid Phases.*** Identification of the solid phases was carried out by an X-ray method using the X- ray diffractometer HZG-4/A-2 (GDR) with continuous registration. The qualitative analysis was based on the distribution curves of the dispersed radiation intensity expressed as $I = f(\theta)$. All diffractograms were inspected for the series of interplanar distance, $d$, and the relative intensities, $I$, and compared with the numeric data listed in “The powder diffraction file” and “Rentgenostrukturalne metody identyfikacji minerałów i skał”.[15,16]

## Results and Conclusion

The comparison of literature data with the present work for the binary system NaCl + $H_2O$ in the temperature range 293−323 K is presented in Table 1.

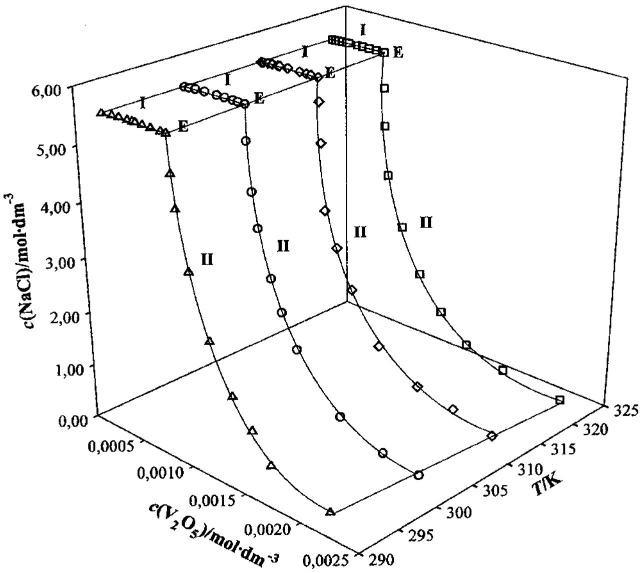

**Figure 1.** Solubility of NaCl and $V_2O_5$ in the system NaCl + $V_2O_5$ + $H_2O$: △, 293 K; ○, 303 K; ◇, 313 K; □, 323 K.

Data derived from the quantitative chemical analysis of the equilibrium solutions are included in Table 2.

The collected data gave grounds for the construction of a part of the polythermal solubility surface for the NaCl + $V_2O_5$ + $H_2O$ system (Figure 1).

Each respective isotherm is composed of two branches. Branch I (Figure 1) of each isotherm describes the sodium chloride concentration changes with increasing concentration of $V_2O_5$ in equilibrium solution. Branches II of the isotherms represent the concentration changes of $V_2O_5$ with increasing concentration of NaCl in solution and correspond to the saturated solution of $V_2O_5$.

Figure 1 consists of the field of unsaturated solutions extending from the origin to the solubility surfaces, surface I representing saturated solutions with solid-phase NaCl, and surface II representing saturated solutions with solid-phase $V_2O_5$. There is also a eutonic line representing doubly-saturated solutions with NaCl and $V_2O_5$ as the equilibrium solid phases.

The increase in vanadium concentration values toward the eutonic points E implies a very insignificant influence on the sodium chloride solubility in equilibrium solution. The detected difference in the NaCl solubility values in aqueous solution and in the eutonic points is measured to be −0.045 mol·dm$^{-3}$ at $T$ = 293 K; −0.037 mol·dm$^{-3}$ at 303 K; −0.028 mol·dm$^{-3}$ at 313 K; and −0.027 mol·dm$^{-3}$ at 323 K, respectively. This increment in the NaCl solubility is linked with the vanadium presence in solution and is decreased with the temperature rise.

On the basis of plotted curves (Figure 1) and data analysis (Table 2), it was concluded that the solubility values of NaCl and $V_2O_5$ change only insignificantly with the temperature rise.

Analysis of the data collected in Table 2 revealed that, in the case of each studied temperature, the densities of saturated equilibrium solutions of NaCl are practically constant with the increase in vanadium concentration values in solution. When the specific eutonic points E are crossed over, the solution density values are rapidly diminished to reach the values which correspond to the density values of $V_2O_5$ saturated solutions.

**Table 3. Interplanar Distance, *d*, and the Relative Intensities, *I*, for $V_2O_5$ (Radiation Cu Kα, $\lambda$ = 0.154 18 nm)**

| exp data | | lit. data | | exp data | | lit. data | |
|---|---|---|---|---|---|---|---|
| *d*/(nm) | I | *d*/(nm) | I | *d*/(nm) | I | *d*/(nm) | I |
| 0.573 | 35 | 0.570 | 33 | 0.192 | 15 | 0.192 | 13 |
| 0.436 | 100 | 0.438 | 100 | 0.186 | 10 | 0.186 | 7 |
| 0.340 | 86 | 0.339 | 83 | 0.178 | 11 | 0.177 | 10 |
| 0.287 | 51 | 0.287 | 53 | 0.165 | 9 | 0.165 | 7 |
| 0.276 | 17 | 0.276 | 13 | 0.157 | 8 | 0.156 | 7 |
| 0.268 | 10 | 0.268 | 7 | 0.151 | 8 | 0.151 | 7 |
| 0.261 | 18 | 0.261 | 13 | 0.149 | 8 | 0.149 | 7 |
| 0.218 | 10 | 0.218 | 7 | 0.145 | 8 | 0.145 | 7 |
| 0.199 | 9 | 0.199 | 7 | 0.131 | 8 | 0.131 | 7 |

An X-ray analysis of the solid phase confirms that, within the temperature range studied, the equilibrium solid phase along branch I is NaCl, while along branch II it is $V_2O_5$. Along the eutonic line, both these solid phases occur.

Table 3 gives the *d*-spacing for $V_2O_5$ calculated from the diffraction angles using the Bragg equation.

## Literature Cited

(1) Trypuć, M.; Torski, Z. Investigations on the optimum conditions of NaCl conversion into $NaVO_3$. *Ind. Eng. Chem. Res.* **1998**, *37*, 1095−1098.
(2) Trypuć, M.; Torski, Z. Conversion rate of NaCl into $NaVO_3$ in the presence of $V_2O_5$ and steam. *Pol. J. Appl. Chem. Res.* **1996**, *3*, 301−306.
(3) Aarts, W. H. Process for the production of sodium carbonate and hydrochloric acid and/or chlorine. U.S. Patent 3313593, 1967.
(4) Niederliñski, A.; Bukowski, A.; Koneczny, H. *Soda i produkty towarzyszıce*; WNT: Warsaw, Poland, 1978.
(5) Bortel, E.; Koneczny, H. *Zarys technologii chemicznej;* PWN: Warsaw, Poland, 1992.
(6) Trypuć, M.; Torski, Z. The investigations on the synthesis of $NaVO_3$ and HCl from NaCl and $V_2O_5$ in the presence of steam. *Przem. Chem.* **1997**, *7*, 319−320.
(7) Trypuć, M.; Białowicz, K.; Mazurek, K. Solubility on the Synthesis of $NaVO_3$ and $Cl_2$ from NaCl and $V_2O_5$ in the Presence of Oxygen. *Ind. Eng. Chem. Res.* **2001**, *40*, 731−735.
(8) Cohen-Adad, R.; Lorimer, J. W. *Alkali metal and Ammonium Chlorides in water and $D_2O$*; IUPAC Solubility data series; Pergamon Press: Oxford, 1991; Vol. 47.
(9) Sytniewski, A.; Kawicka, H. Computer interpretation of phase equilibrium of the NaCl − $NH_4Cl$ − $H_2O$ system. *Chem. Stosow.* **1990**, *1−2*, 125−134.
(10) Sytniewski, A. Regression analysis of the salt solubility of the NaCl − $NaHCO_3$ − $H_2O$, $NH_4HCO_3$ − $NaHCO_3$ − $H_2O$ and $NH_4HCO_3$ − $NH_4Cl$ − $H_2O$ systems. *Pol. J. Appl. Chem.* **1998**, *1*, 23−29.
(11) Minczewski, J.; Marczenko, Z. *Chemia analityczna*; PWN: Warsaw, Poland, 1987.
(12) Williams, W. J. *Oznaczanie anionów*; PWN: Warsaw, Poland, 1985.
(13) Struszyñski, M. *Analiza ilościowa i techniczna*; PWN: Warsaw, Poland, 1982.
(14) Sandell, G. *Colorimetric metal analysis*; Interscience Publishers: New York, 1959.
(15) *Powder Diffraction File*; Joint Committee on Powder Diffraction Standards: USA, 1976.
(16) Przybora, E. *Rentgenostruturalne metody identyfikacji minerałów i skał; WG: Warsaw, Poland, 1957.*

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