

# Plotting of the solubility isotherm for the $\text{NH}_4\text{NO}_3 + \text{NaVO}_3 + \text{H}_2\text{O}$ system

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The equilibrium research was performed for the  $\text{NH}_4\text{NO}_3 + \text{NaVO}_3 + \text{NH}_4\text{VO}_3 + \text{NaNO}_3 + \text{H}_2\text{O}$  system at 293 and 303 K. The location of the  $P_1$  and  $P_2$  triple points was determined on the equilibrium plots with the planar projection according to Jänecke method. The maximum yield of the conversion of ammonium nitrate(V) to ammonium vanadate(V) was calculated at  $P_1$  points. The results constitute the basis to design further equilibrium experiments aimed to precisely determine the lines separating the areas of the co-crystallization of salts in the investigated system on the equilibrium plots in the oblique projection on a plane according to Jänecke method.

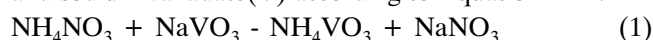
**Keywords:** SCS method, equilibrium investigation, double exchange, ammonium nitrate(V), ammonium vanadate(V).

## INTRODUCTION

Production of sodium carbonate with the Soda-Chlorine-Saltpetre method (SCS) gives valuable by-products – chlorine and solution of ammonium-sodium saltpetre composed of 80%  $\text{NH}_4\text{NO}_3$ ; 18%  $\text{NaNO}_3$  and 2%  $\text{NaCl}$  as recalculated to solids<sup>1</sup>. That solution is a material for the production of nitrogenous fertilizer. Authors of the SCS method had assumed processing of that liquor by the evaporation and crystallization of ammonium-sodium saltpetre. That way is difficult due to a possibility of the uncontrolled decomposition of ammonium nitrate(V) which is catalyzed by the chloride ions remaining in the solution of sodium nitrate(V) after oxidation of sodium chloride with the nitric acid<sup>1-3</sup>.

The equilibrium research on the  $\text{NH}_4\text{NO}_3 + \text{NaVO}_3 + \text{H}_2\text{O}$  system of the exchange salts is performed to develop the new method of utilizing the post-filtration liquor from the SCS method and to avoid the risk of explosion during the further processing of that solution<sup>4-6</sup>.

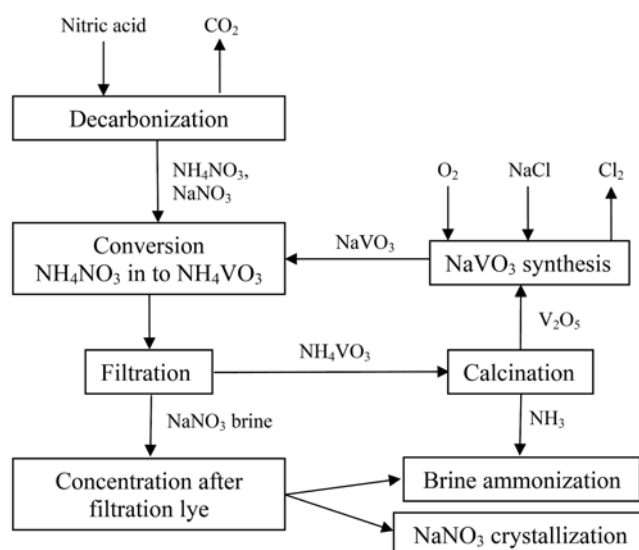
Utilization of the post-filtration liquor is based on a reaction of the double exchange between ammonium nitrate(V) and sodium vanadate(V) according to Equation 1<sup>4-6</sup>.



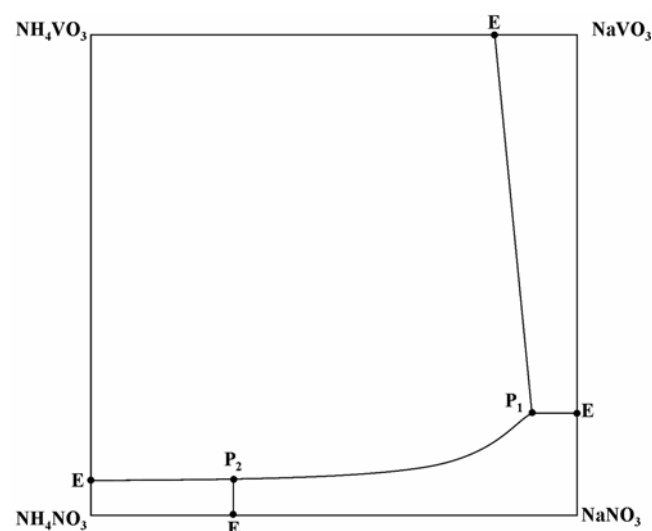
That reaction gives the sparingly soluble ammonium vanadate(V) in a sodium nitrate(V) solution. After the filtration of ammonium vanadate(V), the solution is subjected to concentration and sodium nitrate(V) is crystallized, which eliminates the risk of explosion. Depending on the needs of the soda process, the concentrated solution of sodium nitrate(V) might be directed to the ammonization step and subsequently to carbonization to give sodium bicarbonate<sup>4-6</sup>.

The chemical flow diagram of the conversion of ammonium nitrate(V) with the use of sodium vanadate(V) is presented in Figure 1.

Determination of the equilibrium of the reaction described with Equation 1 requires the construction of the equilibrium plot for the  $\text{NH}_4\text{NO}_3 + \text{NaVO}_3 + \text{NH}_4\text{VO}_3 + \text{NaNO}_3 + \text{H}_2\text{O}$  system, prepared as a planar projection according to the Jänecke method. For that it is necessary to determine the lines separating the areas of the co-crystallization of salts and the triple points for the above quaternary system, as well as the eutonic points for the ternary sub-systems, which in



**Figure 1.** A chemical flow diagram of the conversion of ammonium nitrate(V) to ammonium vanadate(V)



**Figure 2.** A hypothetical equilibrium plot for the quaternary system in a planar projection prepared according to the Jänecke method

the planar projection correspond to the edges of the square of the equilibrium plot. The hypothetical equilibrium plot obtained according to the Jänecke method is shown in Figure 2.

The preliminary equilibrium research for the  $\text{NH}_4\text{NO}_3 + \text{NaVO}_3 + \text{NH}_4\text{VO}_3 + \text{NaNO}_3 + \text{H}_2\text{O}$  system at 293 and 303 K was performed to determine:

- location of the triple points  $P_1$  and  $P_2$  on the plot obtained for the investigated system with the Jänecke method,
- yield of the conversion of ammonium nitrate into ammonium vanadate(V) at  $P_1$  point,
- time of equilibration.

## EXPERIMENTAL

### Reagents

For the research the analytical grade reagents were used:  $\text{NH}_4\text{VO}_3$  (99% Aldrich),  $\text{NaVO}_3$  ( $\geq 98\%$  Fluka),  $\text{NaNO}_3$  and  $\text{NH}_4\text{NO}_3$  (pure for analysis POCH Gliwice).

### Methods

The research was performed with the method of isothermal saturation of solutions. For the  $P_2$  point, the required amounts of ammonium vanadate(V), ammonium nitrate(V), sodium nitrate(V) and water were put into the 100 cm<sup>3</sup> Erlenmeyer flasks. For the  $P_1$  point, which is inconvergently saturated, the excess of sodium nitrate(V), ammonium vanadate(V) and the required amount of water were used. In the double exchange reaction at the  $P_1$  point, ammonium nitrate(V) is transferred to the solution, while sodium vanadate(V) is in the solid phase. The mixtures in the Erlenmeyer flasks were thermostated at the selected temperature and stirred until the equilibrium between phases was reached. The temperature was kept constant with the Polystat CC1 thermostat with the precision of  $\pm 0,02$  K, which was additionally monitored with the mercury thermometer with the  $\pm 0,1$  K precision. The equilibration time was determined experimentally. To do so, for the solution samples were collected in 24 h intervals, the concentrations of sodium and vanadate(V) ions were determined. After equilibrium was reached, the stirring was stopped, and the mixture was left for 24 hours for sedimentation. In the next step, samples of the clear equilibrated solutions were transferred into the Ostwald pycnometer for the density measurements. Density was determined gravimetrically with the precision of  $\pm 0,002$  g·cm<sup>-3</sup>. The pycnometer contents was subsequently transferred quantitatively into the 500 cm<sup>3</sup> measuring flask and diluted with the re-distilled water. The solutions were analyzed to determine the concentration of sodium, vanadate(V), ammonium and nitrate ions.

### Analytical methods

The amount of sodium ions was determined with the Kolthoff and Barber gravimetric method as a precipitate of sodium-zinc-uranyl acetate<sup>7</sup>.

The amount of ammonium ions was determined alkalimetrically with the formalin method<sup>7</sup>. Ammonium ions react with formaldehyde to form hexamethylenetetramine and the corresponding amount of acid, which is titrated with the standard solution of sodium hydroxide in the presence of phenolphthalein.

The amount of nitrate and ammonium ions was determined as total ammonia with the distillation method in sodium hydroxide with the Devard alloy used as a reducing agent<sup>7</sup>. Ammonia was absorbed in the standard solution of sulfuric acid, its excess was then titrated with the standard

solution of sodium hydroxide in the presence of methyl red. The concentrations of nitrate and ammonium ions were calculated from the following equations:

$$- [\text{NH}_4^+] = \frac{1}{2} ([\text{NH}_3] - [\text{Na}^+] + [\text{VO}_3^-])$$

$$- [\text{NO}_3^-] = \frac{1}{2} ([\text{NH}_3] + [\text{Na}^+] - [\text{VO}_3^-])$$

The concentration of vanadium(V) in the solutions was determined spectrophotometrically as a complex with 4-(2-pyridylazo) resorcinol at the wavelength of 540 nm with the double-beam Hitachi U-2000 UV/Vis spectrophotometer, 10 mm quartz absorption cells were used. The molar absorption coefficient is  $3.5 \cdot 10^4 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ <sup>8</sup>.

## Discussion

Determination of the time dependence of the concentrations of vanadate(V) and sodium ions for  $P_1$  points at 293 K revealed that the equilibrium between the solid phase and the solution is reached after 200 h. Figure 3 presents the changes of vanadate(V) ion concentration as a function of time, and Figure 4 presents the similar dependence for the sodium ion concentration. Curves on Figures 3 and 4 reveal a decrease of concentration of both ions until the equilibrium is reached. Such a dependence indicates that at the  $P_1$  point the reaction in the system is opposite to that described with Equation 1.

The experimental data on the mutual solubility of salts at  $P_1$  and  $P_2$  points for the investigated system were used to calculate the mole fractions of ammonium and vanadate(V) ions in the equilibrium solutions and further to determine the yield of conversion of ammonium nitrate(V) to ammo-

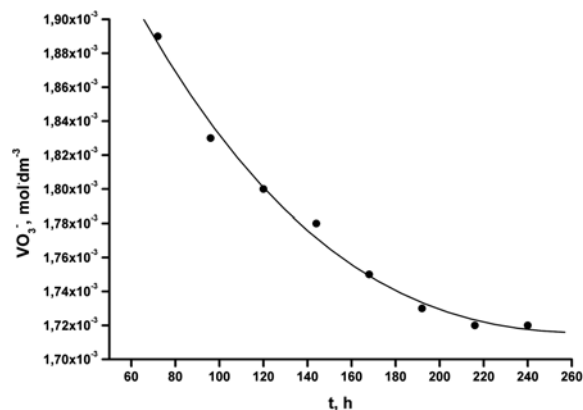


Figure 3. Changes of the vanadate(V) ion concentration during equilibration at  $P_1$  point at 293 K

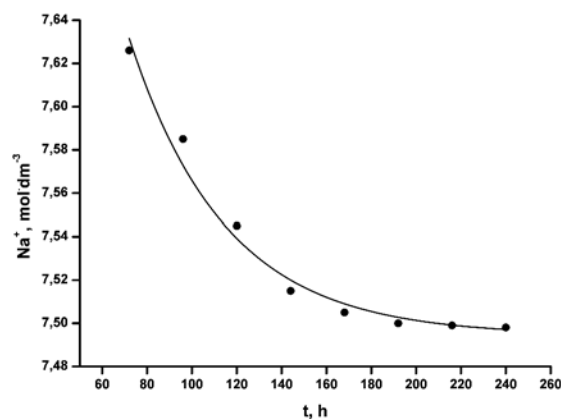


Figure 4. Changes of the sodium ion concentration during equilibration at  $P_1$  point at 293 K

**Table 1.** The mutual solubility data for the  $\text{NH}_4\text{NO}_3 + \text{NaVO}_3 + \text{NH}_4\text{VO}_3 + \text{NaNO}_3 + \text{H}_2\text{O}$  system

	$d$ ( $\text{g}\cdot\text{cm}^{-3}$ )	$\text{NH}_4^+$ ( $\text{mol}\cdot\text{dm}^{-3}$ )	$\text{Na}^+$ ( $\text{mol}\cdot\text{dm}^{-3}$ )	$\text{NO}_3^-$ ( $\text{mol}\cdot\text{dm}^{-3}$ )	$\text{VO}_3^-$ ( $\text{mol}\cdot\text{dm}^{-3}$ )	$x$ $\text{NH}_4^+$	$x$ $\text{VO}_3^-$
T = 293 K							
$E_1^5$	1.392	0	7.165	7.164	$1.5\cdot 10^{-3}$	0	$2.1\cdot 10^{-4}$
$E_2$	1.305	10.532	0	10.532	$4.5\cdot 10^{-5}$	1	$4\cdot 10^{-6}$
$E_3^9$	1.138	0.265	1.350	0	1.615	0.164	1
$E_4^4$	1.439	8.853	4.131	12.984	0	0.682	0
$P_1$	1.381	0.514	7.498	8.010	$1.7\cdot 10^{-3}$	0.064	$2.2\cdot 10^{-4}$
$P_2$	1.432	8.679	3.765	12.444	$4.4\cdot 10^{-5}$	0.697	$4\cdot 10^{-6}$
T = 303 K							
$E_1^5$	1.417	0	7.843	7.841	$1.9\cdot 10^{-3}$	0	$2.4\cdot 10^{-4}$
$E_2$	1.325	11.421	0	11.425	$7.2\cdot 10^{-5}$	1	$6\cdot 10^{-6}$
$E_3^9$	1.170	0.352	1.620	0	1.972	0.179	1
$E_4^4$	1.451	9.733	3.750	13.483	0	0.722	0
$P_1$	1.401	0.606	7.763	8.365	$4.4\cdot 10^{-3}$	0.072	$5.3\cdot 10^{-4}$
$P_2$	1.452	9.640	3.530	13.170	$7.0\cdot 10^{-5}$	0.732	$5\cdot 10^{-6}$

mium vanadate(V). The data on the solution density, concentrations of different ions and the mole fractions are presented in Table 1. Table 1 also contains the data characterizing the eutonic points for the ternary sub-systems, where:

–  $E_1$  – eutonic point for the  $\text{NaVO}_3 + \text{NaNO}_3 + \text{H}_2\text{O}$  system,

–  $E_2$  – eutonic point for the  $\text{NH}_4\text{NO}_3 + \text{NH}_4\text{VO}_3 + \text{H}_2\text{O}$  system,

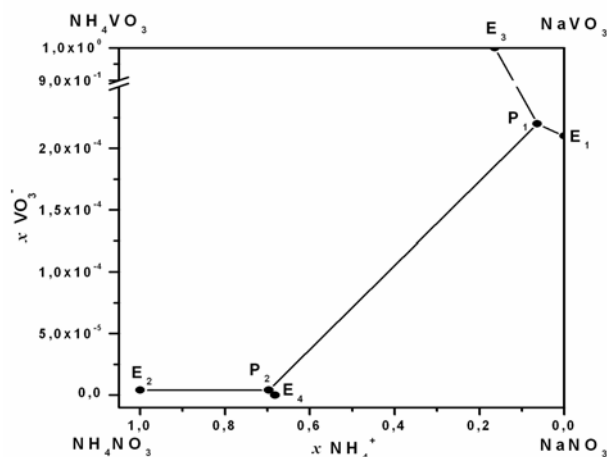
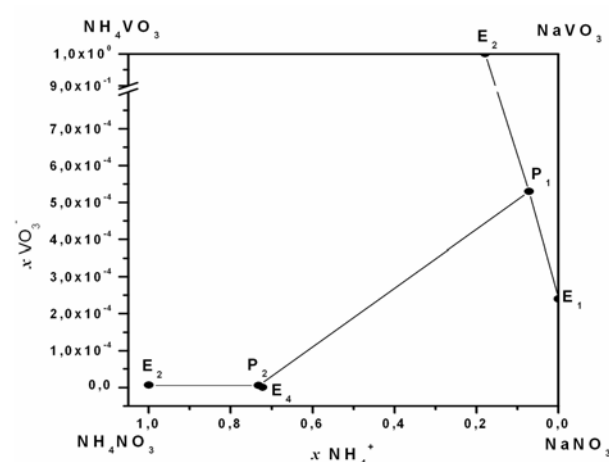
–  $E_3$  – eutonic point for the  $\text{NH}_4\text{VO}_3 + \text{NaVO}_3 + \text{H}_2\text{O}$  system,

–  $E_4$  – eutonic point for the  $\text{NaNO}_3 + \text{NH}_4\text{NO}_3 + \text{H}_2\text{O}$  system.

Mole fractions of ammonium and vanadate(V) ions without taking into account the solvent, were calculated from the following formulas:

$$x_{\text{NH}_4^+} = \frac{[\text{NH}_4^+]}{[\text{NH}_4^+] + [\text{Na}^+]}; x_{\text{VO}_3^-} = \frac{[\text{VO}_3^-]}{[\text{VO}_3^-] + [\text{NO}_3^-]}$$

Based on the experimental data tabulated in Tab. 1, the equilibrium plots were prepared as a planar projection according to the Jänecke method for 293 and 303 K (Figures 5 and 6). The experimental data indicate that at 293 and 303 K the  $P_1$  point is inconvergently saturated and is located in a triangle determined by the corners corresponding to the pure  $\text{NH}_4\text{VO}_3$ ,  $\text{NaNO}_3$  and  $\text{NH}_4\text{NO}_3$ . Figures 5 and 6 reveal that  $P_1$  is apparently positioned in the triangle determined by  $\text{NaVO}_3$ ,  $\text{NaNO}_3$  i  $\text{NH}_4\text{VO}_3$  salts, which suggests

**Figure 5.** The equilibrium plot prepared according to the Jänecke method for the  $\text{NH}_4\text{NO}_3 + \text{NaVO}_3 + \text{NH}_4\text{VO}_3 + \text{NaNO}_3 + \text{H}_2\text{O}$  system at 293 K**Figure 6.** The equilibrium plot prepared according to the Jänecke method for the  $\text{NH}_4\text{NO}_3 + \text{NaVO}_3 + \text{NH}_4\text{VO}_3 + \text{NaNO}_3 + \text{H}_2\text{O}$  system at 303 K

its convergently saturated relative to the solid phase. That results from the appropriate set of the scale of axis with the mole fraction of vanadates(V), due to the very limited solubility of sodium and ammonium vanadates(V) in the saturated solutions of sodium nitrate(V) and ammonium nitrate(V).

The maximum yield of conversion of ammonium nitrate(V) to ammonium vanadate(V) was determined based on the mole fractions of ammonium ions in the equilibrium solutions at  $P_1$  points. For 293 and 303 K, the yields calculated with respect to the ammonium ions are 93,6% and 92,8%, respectively. The reaction yield was calculated from the following equation:

$$W_{\text{NH}_4^+} = (1 - x_{\text{NH}_4^+}) \cdot 100\%$$

## CONCLUSIONS

The preliminary research on equilibrium in the  $\text{NH}_4\text{NO}_3 + \text{NaVO}_3 + \text{NH}_4\text{VO}_3 + \text{NaNO}_3 + \text{H}_2\text{O}$  system reveals a strong salting out effect of sodium and ammonium nitrates(V) on vanadates(V). That positively affects the precipitation of ammonium vanadate(V). Only insignificant influence of temperature on the yield of conversion of ammonium nitrate(V) to ammonium vanadate(V) was found. The increase of temperature by 10 K results in the yield decrease by 0,8%.

## ACKNOWLEDGMENT

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