

Utilization of the post-filtration lye from the SCS method of soda production

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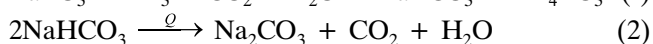
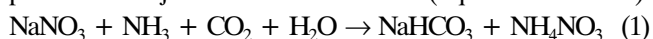
The mutual solubility of salts in the $\text{NaVO}_3\text{-NaNO}_3\text{-H}_2\text{O}$ system was investigated at 293 – 323 K temperature range by the method of isothermal saturation of solutions. A fragment of the solubility polytherm for that system was plotted, based on the obtained data. The investigated system is a part of the quaternary $\text{NH}_4\text{NO}_3\text{-NaVO}_3\text{-NH}_4\text{VO}_3\text{-NaNO}_3$ system, and it is necessary for plotting the solubility isotherm as a planar projection according to Janecke, since it defines one edge of its square. Knowledge of the isotherm for that quaternary system is necessary to determine the optimal utilization conditions for the post-filtration lye, formed during the soda production from NaNO_3 by the Solvay method, using NaVO_3 .

Keywords: mutual solubility, sodium metavanadate, sodium nitrate, ternary system.

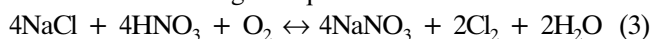
Presented at VII Conference Wasteless Technologies and Waste Management in Chemical Industry and Agriculture, Międzyzdroje, 12 – 15 June, 2007.

INTRODUCTION

The SCS method (Soda-Chlorine-Saltpetre) is a modification of the classic Solvay method of soda production^{1,2}. Generally, it is based on the carbonization of the ammoniated NaNO_3 brine. Sodium bicarbonate obtained in that process is subjected to calcination^{1–3} (equations 1 and 2).



Sodium nitrate required for that process is obtained in a reaction of the oxidation of solid sodium chloride with nitric acid according to equation 3.



After the filtration of sodium bicarbonate sediment, the lye is obtained, with the composition depending on the carbonization conditions. The major components of that lye are ammonium nitrate (ca. 80%), unreacted sodium nitrate 18% and sodium chloride from the oxidation process 2%, as recalculated to the solid mass^{1,2}.

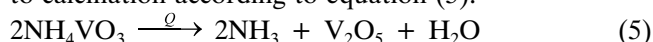
So far it has been suggested that the lye might be used as a raw material for the production of mixed ammonium-sodium saltpetre, which is a nitrogenous fertilizer^{1,2}. However, concentration of that solution for crystallizing the salts is difficult due to the explosive properties of ammonium nitrate. The presence of chlorides catalyzing the uncontrolled decomposition of ammonium nitrate^{4,5}, is especially disadvantageous.

The aim of the research is to eliminate the danger occurring during the recovery of solid ammonium-sodium nitrate by the evaporation of the post-filtration solution in the process of soda production with the SCS method, as well as to improve the material and economical efficiency of that method.

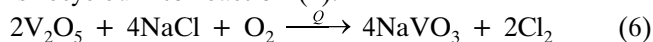
The research on partial utilization of the post-filtration lye from the classic Solvay method, indicates the possibility of the use of sodium vanadate(V) instead of calcium hydroxide suspension^{6,7}. That approach to the utilization of the post-filtration lye from the SCS method is based on a reaction of sodium vanadate(V) with ammonium nitrate, present in the solution, according to equation⁴.



After the reaction, the precipitated sparingly soluble ammonium vanadate is washed with water and subjected to calcination according to equation (5).



Ammonia from reaction (5) is recycled to the step of ammonization of sodium nitrate brine, while vanadium(V) oxide reacts with sodium chloride in the presence of oxygen⁸ (equation 6) forming sodium vanadate(V), which is recycled into reaction (4).



The solution after the filtration of NH_4VO_3 contains the remaining sodium nitrate. That lye is concentrated, saturated with solid sodium nitrate, and then recycled into the step of ammonization of the NaNO_3 brine. The previous research^{1,2} indicated that the small amount of sodium chloride does not have the negative effect on the production of NaHCO_3 .

Utilization of the post-filtration lye from the SCS method with sodium vanadate(V) improves the material and the economic efficiency of the soda production by:

- recovery of sodium nitrate, which circulates in the closed cycle, which results in the smaller use of nitric acid required for the production of that reagent,
- limiting the chlorine production, resulting from the amount of the recycled unreacted sodium nitrate in the process of NaHCO_3 production,
- practically a complete recovery of ammonia, which circulates in the closed cycle.

The economical control of the utilization of the post-filtration lye from the SCS method with the use of NaVO_3 requires precise knowledge of the equilibrium plot for the

$\text{NH}_4\text{NO}_3\text{-NaVO}_3\text{-H}_2\text{O}$ reciprocal salt pairs system in the planar projection according to Janecke. Such plotting of the isotherm requires a research on equilibrium in four ternary subsystems: $\text{NaNO}_3\text{-NaVO}_3\text{-H}_2\text{O}$, $\text{NH}_4\text{NO}_3\text{-NH}_4\text{VO}_3\text{-H}_2\text{O}$, $\text{NaNO}_3\text{-NH}_4\text{NO}_3\text{-H}_2\text{O}$, $\text{NaVO}_3\text{-NH}_4\text{VO}_3\text{-H}_2\text{O}$, which are positioned on the respective edges and inside the square equilibrium plot, to determine the border lines limiting the areas of co-crystallization of specific salts and the triple points.

The literature data on the ternary systems mentioned above are incomplete, and there are no reports on the

quaternary system. The complete data have been found only for the

$\text{NaVO}_3\text{-NH}_4\text{VO}_3\text{-H}_2\text{O}$ system at 293 – 323 K⁹, while partial data are available for the $\text{NaNO}_3\text{-NH}_4\text{NO}_3\text{-H}_2\text{O}$ system². Therefore, we decided to investigate the mutual solubility of NaVO_3 and NaNO_3 in water at 293 – 323K temperature range.

EXPERIMENTAL

Reagents

In the research, the analytical grade reagents were used, NaVO_3 (≥ 98 wt.% Fluka), NaNO_3 (pure for analysis POCH Gliwice).

Method

Determination of the mutual solubility in the $\text{NaNO}_3\text{-NaVO}_3\text{-H}_2\text{O}$ system was performed at 293, 303, 313 and 323 K, with the method of the isothermal saturation of solutions. The required amounts of components, one of which was in excess relative to its solubility in water, were put into the 100 cm³ Erlenmeyer flasks with 80 cm³ of the re-distilled water. Then the flasks were put into the water thermostat and stirred with the magnetic stirrer. The required temperature was maintained with the Polystat CC1 thermostat, with a ± 0.02 K precision, controlled with the mercury thermometer with the ± 0.1 K precision. The time of equilibration between the solid and liquid phases was determined experimentally as 100 h. After that time the stirring was stopped, and after the sedimentation for 1 h, the samples of clean equilibrated solution were transferred into the pre-calibrated Ostwald pycnometer for the density measurements. The density was determined gravimetrically with the precision of ± 0.002 g·cm⁻³. The samples were collected under the pressure increased with the use of a micrometering pump, which prevented the crystallization of the solution components, especially at higher temperatures. The pycnometer contents was subsequently transferred quantitatively into a measuring flask and diluted to 500 cm³ with the re-distilled water. The composition of the obtained solutions was determined during the chemical analyses. The concentration of sodium and vanadate ions was determined.

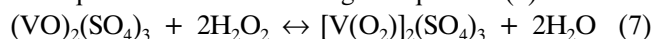
Three independent analyses were performed for each collected sample. The precision of the analyses was estimated by the Relative Standard Deviation (RSD) error, which had not exceeded 2%. The nitrate concentration was calculated based on the difference between the concentrations of sodium and vanadate ions.

Analytical methods

The concentration of sodium ions in the equilibrated solutions was determined gravimetrically with the Kolthoff and Barber method as sodium-zinc-uranyl acetate^{10, 11}.

Vanadium(V) was determined spectrophotometrically as a complex with the hydrogen peroxide. The analyses were performed with the double-beam UV-VIS Hitachi U-2000 spectrophotometer in the quartz cells with the 10 mm optical way. Vanadium(V) in the concentrated sulfuric acid (1:3) in a presence of 3 wt.% aqueous solution of H_2O_2 forms the compounds $\text{V}(\text{O}_2)\text{X}_3$ and/or $\text{V}(\text{O}_2)\text{X}_5^{2-}$,

where X is the monovalent anion. That reaction goes in the equimolar ratio according to equation (7)¹¹.



These compounds reveal maximum absorbancy at 450 nm, and the molar absorbancy is 300 dm³·mol⁻¹·cm⁻¹. The system obeys the Beer law in a broad range of concentrations between $8 \cdot 10^{-3}$ and 2 mol·dm⁻³¹¹.

For the solutions with very low concentration, below $2 \cdot 10^{-2}$ mol·dm⁻³, the spectrophotometric method with 4-(2-pyridylazo)resorcinol (PAR) was used. The analyses were performed with the double-beam UV-VIS Hitachi U-2000 spectrophotometer in the quartz cells with the 10 mm optical way. At pH 5-6 vanadium(V) compounds form complexes with PAR with the maximum absorbancy at 540 nm. The maximum color saturation appears after 30 min, and remains steady for 2 hours. The molar absorbancy is $3.6 \cdot 10^4$ dm³·mol⁻¹·cm⁻¹¹¹.

For the selected experimental points, the analyses of the solid phase were performed with the X-ray powder diffractometer Philips X-Pert PRO System. To determine the solid phase composition, the diffraction data were compared to the standards included in the „Powder Diffraction File”¹².

RESULTS AND DISCUSSION

The experimental data on the mutual solubility of NaVO_3 and NaNO_3 in the

$\text{NaVO}_3\text{-NaNO}_3\text{-H}_2\text{O}$ system are presented in Table 1. For four temperatures, the equilibrium concentrations of salts in mol·dm⁻³, the density of the equilibrated solutions in g·cm⁻³ and the molar ratios, without taking into account the solvent and the solid phase composition, are tabulated.

The molar ratios, without taking into account the solvent, were calculated as follows:

$$X_{\text{NaVO}_3} = \frac{[\text{NaVO}_3]}{[\text{NaVO}_3] + [\text{NaNO}_3]}, X_{\text{NaNO}_3} = \frac{[\text{NaNO}_3]}{[\text{NaVO}_3] + [\text{NaNO}_3]}$$

A fragment of the polytherm for the investigated system was plotted for the temperature range 293 – 323 K, based on the data from Table 1, and presented in Figures 1 and 2. Figure 1 presents the branches II of the solubility isotherms, that correspond to the solutions saturated with sodium vanadate(V). Their characteristic course indicates

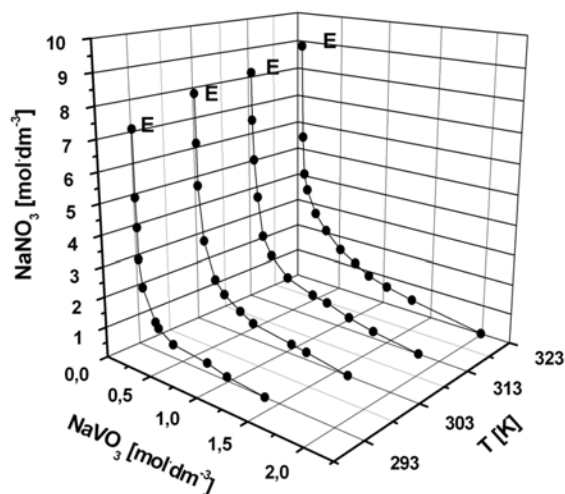


Figure 1. Branches II of the solubility isotherms for $\text{NaVO}_3\text{-NaNO}_3\text{-H}_2\text{O}$ system

Table 1. The solubility in the NaVO₃ – NaNO₃ – H₂O system

No.	ρ (g·cm ⁻³)	c (mol·dm ⁻³)		x		Solid phase composition
		NaVO ₃	NaNO ₃	NaVO ₃	NaNO ₃	
T = 293 K						
1	1.392	0	7.317	0	1	NaNO ₃
2	1.390	0.003	7.255	0.0002	0.9998	NaNO ₃
3	1.392	0.009	7.176	0.0007	0.9993	NaNO ₃
4 (E)	1.392	0.013	7.099	0.0010	0.9990	NaNO ₃ + NaVO ₃
5	1.254	0.016	4.910	0.0021	0.9979	NaVO ₃
6	1.195	0.027	3.934	0.0049	0.9951	NaVO ₃
7	1.154	0.028	2.883	0.0075	0.9925	NaVO ₃
8	1.112	0.066	1.976	0.0277	0.9723	NaVO ₃
9	1.069	0.203	0.958	0.1668	0.8332	NaVO ₃
10	1.063	0.236	0.780	0.2254	0.7746	NaVO ₃
11	1.060	0.398	0.436	0.4797	0.5203	NaVO ₃
12	1.088	0.775	0.303	0.7325	0.2675	NaVO ₃
13	1.108	0.982	0.130	0.8937	0.1063	NaVO ₃
14	1.118	1.360	0	1	0	NaVO ₃
T = 303 K						
1	1.412	0	7.890	0	1	NaNO ₃
2	1.412	0.003	7.877	0.0002	0.9998	NaNO ₃
3	1.412	0.008	7.862	0.0005	0.9995	NaNO ₃
4 (E)	1.417	0.019	7.824	0.0013	0.9987	NaNO ₃ + NaVO ₃
5	1.307	0.027	6.165	0.0026	0.9974	NaVO ₃
6	1.253	0.033	4.731	0.0048	0.9952	NaVO ₃
7	1.155	0.092	2.850	0.0251	0.9749	NaVO ₃
8	1.108	0.216	1.601	0.1080	0.8920	NaVO ₃
9	1.092	0.318	1.193	0.2003	0.7997	NaVO ₃
10	1.084	0.496	0.800	0.3807	0.6193	NaVO ₃
11	1.090	0.640	0.541	0.5499	0.4501	NaVO ₃
12	1.110	1.049	0.321	0.7825	0.2175	NaVO ₃
13	1.114	1.201	0.246	0.8462	0.1538	NaVO ₃
14	1.135	1.609	0	1	0	NaVO ₃
T = 313 K						
1	1.418	0	8.298	0	1	NaNO ₃
2	1.418	0.014	8.268	0.0009	0.9991	NaNO ₃
3	1.418	0.024	8.200	0.0015	0.9985	NaNO ₃
4 (E)	1.419	0.037	8.178	0.0023	0.9977	NaNO ₃ + NaVO ₃
5	1.270	0.040	6.523	0.0035	0.9965	NaVO ₃
6	1.220	0.059	5.108	0.0074	0.9926	NaVO ₃
7	1.204	0.097	3.783	0.0186	0.9814	NaVO ₃
8	1.141	0.156	2.386	0.0517	0.9483	NaVO ₃
9	1.114	0.256	1.754	0.1152	0.8848	NaVO ₃
10	1.098	0.442	1.124	0.2739	0.7261	NaVO ₃
11	1.107	0.728	0.803	0.4808	0.5192	NaVO ₃
12	1.107	0.885	0.699	0.5704	0.4296	NaVO ₃
13	1.121	1.118	0.423	0.7442	0.2558	NaVO ₃
14	1.130	1.366	0.229	0.8729	0.1271	NaVO ₃
15	1.150	1.808	0	1	0	NaVO ₃
T = 323 K						
1	1.431	0	8.959	0	1	NaNO ₃
2	1.431	0.011	8.902	0.0006	0.9994	NaNO ₃
3	1.431	0.035	8.837	0.0019	0.9981	NaNO ₃
4 (E)	1.431	0.052	8.819	0.0028	0.9972	NaNO ₃ + NaVO ₃
5	1.268	0.063	5.457	0.0073	0.9927	NaVO ₃
6	1.204	0.082	4.058	0.0143	0.9857	NaVO ₃
7	1.181	0.116	3.478	0.0248	0.9752	NaVO ₃
8	1.144	0.220	2.639	0.0643	0.9357	NaVO ₃
9	1.125	0.345	2.078	0.1268	0.8732	NaVO ₃
10	1.112	0.513	1.509	0.2418	0.7582	NaVO ₃
11	1.110	0.684	1.147	0.3701	0.6299	NaVO ₃
12	1.110	0.839	0.831	0.5100	0.4900	NaVO ₃
13	1.114	1.037	0.623	0.6415	0.3585	NaVO ₃
14	1.130	1.303	0.421	0.7772	0.2228	NaVO ₃
15	1.164	1.987	0	1	0	NaVO ₃

the salting-out effect of sodium nitrate on sodium vanadate(V). The data in Table 1 reveals only the small solubility of NaVO₃ in the saturated NaNO₃ solutions, which is shown in Fig. 2 for better clarity. The course of branches I of isotherms in Fig. 2 are linear with the negative slope, which indicates the small salting-out effect of sodium vanadate(V) on sodium nitrate.

Strong salting-out effect of sodium nitrate on sodium vanadate(V) is advantageous for the reaction (4) equilib-

rium. However, kinetically that effect is undesired. The kinetics of reaction (4) depends on the rate of sodium vanadate(V) solubilization. Due to the reaction progress, the increasing concentration of sodium nitrate results in the decreased rate of sodium vanadate(V) solubilization and slowing down the reaction.

The course of the isotherms in Figures 1 and 2 leads to the preliminary conclusion that no new solid phase is formed in the investigated system. That conclusion might

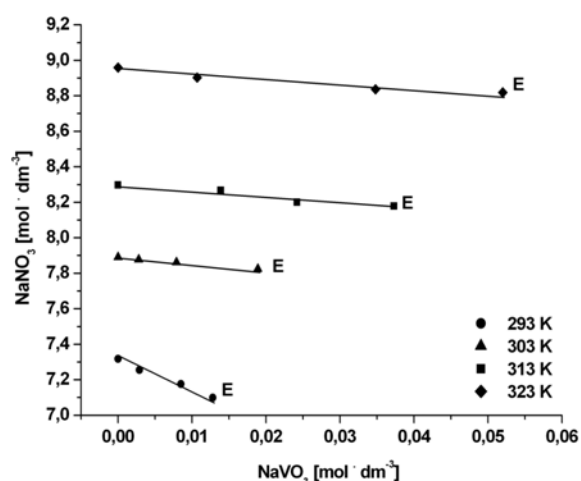


Figure 2. Branches I of the solubility isotherms for the $\text{NaVO}_3\text{-NaNO}_3\text{-H}_2\text{O}$ system

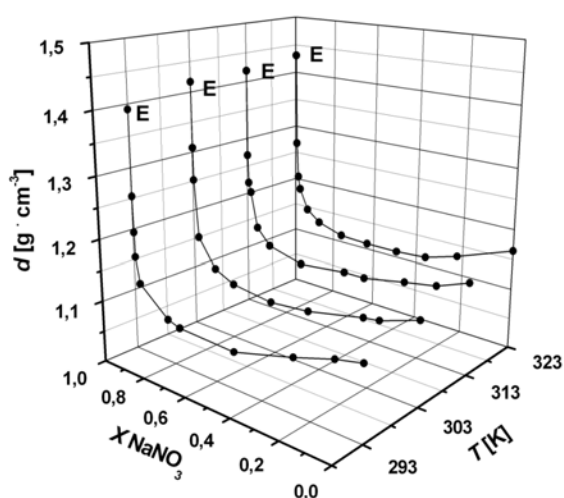


Figure 3. Changes in the density of equilibrium solutions for branches II of the solubility isotherms at temperatures 293 – 323K

be confirmed by constructing the property-composition equilibrium plot, such as the viscosity or density of the equilibrated solutions as a function of concentration of one component expressed as the molar ratio. If the new phase were to be formed, such a plot would reveal characteristic inflections or breaks¹³.

To confirm that conclusion, the dependence of the density of equilibrated solutions on the molar ratio of sodium nitrate was plotted. For the reasons analogous to those for the solubility polytherms, the dependence is presented in two figures (Figs. 3 and 4). Figure 3 presents the dependence of density of the equilibrated solutions on the molar ratio of sodium nitrate for the solutions saturated with sodium vanadate(V). Figure 4 presents a similar plot for the solutions saturated with sodium nitrate. An analysis of both plots supports the conclusion that in the solid phase there is no component other than NaNO_3 and NaVO_3 . An additional basis for such a conclusion is given by the X-ray diffraction experiments, which excluded the presence of any other component in the solid phase.

CONCLUSIONS

Both the experimental data on the mutual solubility of salts in the investigated system and the literature reports⁹

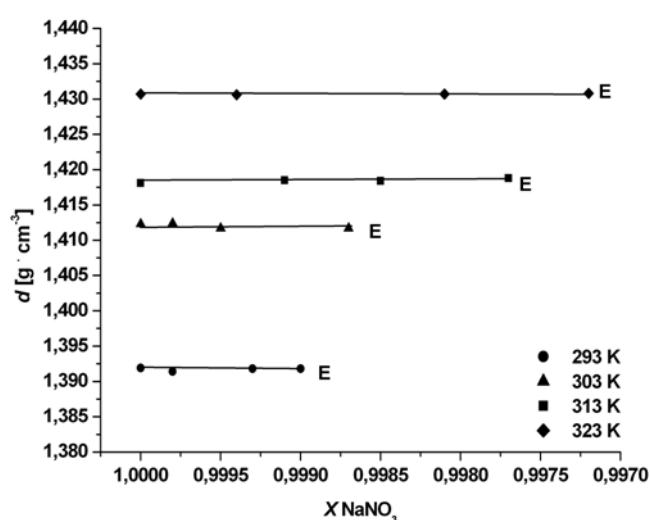


Figure 4. Density changes of the equilibrium solutions for branches I of the solubility isotherms

allow to conclude that the strong salting out effect of sodium nitrate on sodium metavanadate and the NaVO_3 solubility 5 times larger than that of NH_4VO_3 at the eutonic points, are advantageous for the reaction equilibrium (4). According to the obtained results and the literature data⁹ the area of crystallization of sodium nitrate and sodium metavanadate on the Janecke equilibrium plot would be small compared to that for ammonium metavanadate. That indicates that the reaction equilibrium (4) is strongly shifted towards the reaction products, and reaching high efficiency for NH_4VO_3 is possible.

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