Solubility Investigations in the $NH_4Cl + NaVO_3 + NH_4VO_3 + NaCl + H_2O$ System at 303 K

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The mutual salt solubility in the $NH_4Cl + NaVO_3 + NH_4VO_3 + NaCl + H_2O$ system at 303 K was measured using the isothermal solution saturation method. The results were used to plot the solubility isotherms in the oblique projection on plane according to Jänecke's. A thorough knowledge of the isotherm course is crucial to the design of a new method based on utilization of the after-filtration liquor generated from the filtration of $NaHCO_3$ solids in the Solvay process.

Introduction

The total amount of chloride ions introduced into the traditional Solvay process in the form of saturated solutions of sodium chloride (approximately 315 g of $NaCl{\cdot}dm^{-3}$) is inefficiently utilized, is afterward transferred to water reservoirs, and is environmentally hazardous. The maximum of the carbonization yield toward sodium ions W_{Na^+} is estimated to be 70%; thus approximately 30% of the unprocessed sodium chloride is accumulated in liquid wastes derived during the ammonia regeneration step and the residual chloride ions are removed in the form of calcium chloride. Currently, conventional large scale production of Na_2CO_3 is accompanied by large amounts of the undesirable liquid wastes. For example, in Poland 10.6 million tons of liquid wastes are generated annually from only 1 million tons of sodium carbonate.[1]

These disadvantages within the Solvay process led to the development of other modificated routes in order to eliminate the ammonia regeneration step and utilize the enormous quantities of NH_4Cl generated. The possible alternatives include chlorine, hydrogen chloride, and (or) fertilizer production.

The present study combines a very limited literature review[2] and the authors' investigations in an attempt to modify completely or partially the Solvay method, which is based on reaction between NaCl and V_2O_5 as an intermediate reactant in the presence of steam or oxygen.

In the course of these reactions (eqs 1 and 2) $NaVO_3$ and Cl_2 or HCl are generated:[3−5]

$$2NaCl + V_2O_5 + 1/2O_2 \rightarrow 2NaVO_3 + Cl_2\uparrow \qquad (1)$$

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

Sodium metavanadate can be used as a chloride ion free raw material in the modified Solvay process or in processing after-filtration liquors into NH_4VO_3 as described by

$$NH_4Cl + NaVO_3 \rightleftarrows NH_4VO_3 + NaCl \qquad (3)$$

The sparingly soluble NH_4VO_3 that precipitates after filtration is subsequently heated and decomposed according to

$$2NH_4VO_3 \rightarrow V_2O_5 + 2NH_3\uparrow + H_2O \qquad (4)$$

V_2O_5 obtained in the process is afterward turned back to the $NaVO_3$ production stage whereas NH_3 is turned back to the brine ammonization. Solution obtained after the NH_4VO_3 filtration (eq 3) with an addition of solid NaCl is an initial brine for the Na_2CO_3 production process. As outlined above, chloride ions are partly processed into chlorine or hydrogen chloride and vanadium in the form of different chemical compounds is recycled. In general the only limitation of the proposed method is the industry demands for Cl_2 or (and) HCl.

To assign the optimum operating conditions for running the ammonium vanadate production procedure based on the utilization after-filtration liquor, with contents of ammonium chloride and unreacted sodium chloride, a detailed knowledge of the solubility isotherm course in the reciprocal salt pair system $NH_4Cl + NaVO_3 + NH_4VO_3 + NaCl + H_2O$ is required. These isotherms allow for an assessment of the exact location and dimension of the crystallization regions for each respective salt.

Initially, equilibrium studies for four three-component systems were performed. Data for the following systems have been previously reported:

$$NH_4Cl + NH_4VO_3 + H_2O \quad \text{(ref 6)}$$

$$NaVO_3 + NaCl + H_2O \quad \text{(ref 7)}$$

$$NaVO_3 + NH_4VO_3 + H_2O \quad \text{(ref 8)}$$

$$NH_4Cl + NaCl + H_2O \quad \text{(ref 9)}$$

Each of the above systems is located on the particular side of the diagram square in the oblique projection on plane presented by Jänecke. The eutonic points referred to the adequate three-component systems represent the starting points of lines separating the salt crystallization regions.

The main objective of this study was to determine the locus of lines separating the crystallization areas of the respective salts, which compose the solubility isotherm of the title system at 303 K and are located inside the equilibrium diagram square. The temperature of 303 K was chosen with regard to the demanded temperature of after-

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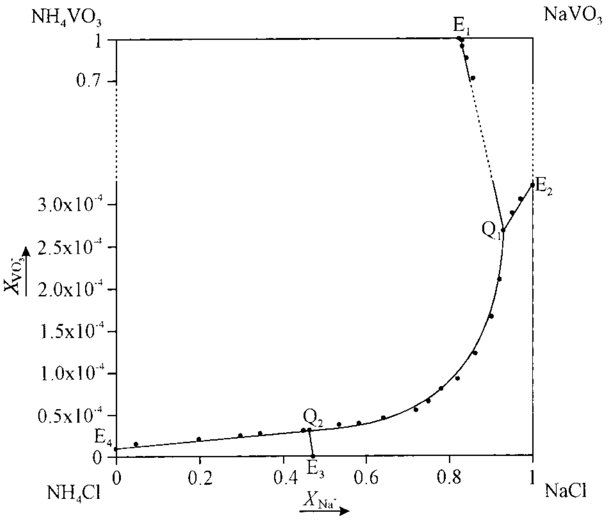

Figure 1. Solubility isotherm of the $NH_4Cl + NaVO_3 + NH_4VO_3 + NaCl + H_2O$ system at 303 K.

filtration liquor in the Solvay method, which is dependent upon ambient temperature.

Experimental Section

The mutual salt solubility was investigated by the method of isothermal solution saturation. The apparatus consisted of Erlenmeyer flasks having a capacity of 100 cm^3, filled with a known amount of salts and distilled water. A typical experimental run can be described as follows. The flasks were placed in a thermostated bath and stirred magnetically. The projected time of thermostating was longer than 1 week due to the slow gaining of the equilibrium state. The temperature control was performed with the precision of ±0.1 K.

After the desired time period, stirring was discontinued and the solution was left for the solid phase to settle. The clear solution was then sampled into calibrated Ostwald pycnometers; the entire content was used, after proper dilution, for the ion concentration determinations.

With regard to system complexity, all experiments were divided into several stages in order to determine the respective isotherm branches and the triple points. The former papers by the authors concerning the three-component systems $NH_4Cl + NH_4VO_3 + H_2O$,[6] $NaVO_3 + NaCl + H_2O$,[7] and $NaVO_3 + NH_4VO_3 + H_2O$,[8] and the reported solubility data for the $NaCl + NH_4Cl + H_2O$[9] system, were used for plotting the equilibrium diagram square (Figure 1) with the location of the respective eutonic points: E_1, E_2, E_3, and E_4. Each of the points is represented by a solution saturated with two salts located on the respective square corners. To reach the locus of the triple points Q_1 or Q_2, a third salt was introduced into solution with a composition defined with the above eutonic points. This procedure was carried out to determine the exact course of the respective segments: E_1Q_1, E_2Q_1, E_3Q_2, and E_4Q_2.

The line marked E_1Q_1, being an isotherm section, was represented by solutions in equilibrium with NH_4VO_3 and $NaVO_3$ salts and determined upon the solution resaturation beginning from the eutonic point E_1 to the triple point Q_1 with increasing mass portions of NaCl.

Line E_2Q_1, being an isotherm section, was represented by solutions in equilibrium with $NaVO_3$ and NaCl salts and assigned upon the solution resaturation with increasing amounts of NH_4VO_3 shifting toward the Q_1 point.

A similar procedure was also reproduced for the locus determination of E_4Q_2 isotherm branch, which separates the crystallization areas of NH_4Cl and NH_4VO_3 salts. Increasing quantities of NaCl were introduced to the saturated solution of a composition defined by E_4, shifting the diagram to the triple point Q_2.

Unfortunately, the position of points located along the line, separating the crystallization areas of NH_4Cl and NaCl—E_3Q_2, were not experimentally found. Even a small amount of NH_4VO_3 introduced to the solution at a composition defined by E_3 rapidly shifted it to the triple point Q_2. This observation implies a very strong salting-out effect of NH_4Cl in the presence of NH_4VO_3.[6]

The line marked Q_1Q_2, being an isotherm section, was represented by solutions in equilibrium with NH_4VO_3 and NaCl and was determined upon the solution resaturation increasing in incremental amounts of NH_4Cl beginning from Q_1 toward Q_2.

All substances used were of analytical purity grade and obtained from the following suppliers: NH_4VO_3 (>99% purity, Aldrich), $NaVO_3$ (>98% purity, Fluka), NH_4Cl (>99.5% purity POCh S.A., Poland) and NaCl (>99.9% purity POCh S.A., Poland).

Chloride, ammonium, and vanadate ion concentration analysis was performed for each sample solution. The concentration of sodium ions was calculated from the difference between anion and cation species existing in solution.

The whole range of chloride ions was determined using the potentiometric method with a fully automatic titrator 716 DMS TITRINO (Methrom, Switzerland) with a combined silver electrode.[10] The average relative error of the measurements was less than 0.3%.

The small concentrations of vanadate ions (<0.2 mol·dm^{-3}) were calculated employing the spectrophotometric method with a double-beam UV/VIS U-2000 HITACHI apparatus. The formation effect of colored complexes by vanadium ions with 4-(2-pyridylazo)resorcinol (PAR)[11,12] was employed. The relative error of the determination was estimated to be less than 1%.

The concentrations of vanadate ions higher than 0.2 mol·dm^{-3} were estimated using the potassium permanganate titration method in the presence of Mohr's salt reducer in acidic conditions.[13] The average relative error was estimated to be less than 0.8%.

The concentration of ammonium ions was measured using the distillation method with the addition of Devarda's alloy, which protected NH_3 from being oxidized to N_2 under the strong influence of VO_3^- ions.[13] The average relative error of the determination was less than 1%.

Additionally, for each solution sample, density measurements were performed by means of a fully automatic Mettler-Toledo DA110M densitometer (Switzerland). The uncertainty was estimated to be ±0.002 g·cm^{-3}. For the whole range of examined concentrations, a qualitative X-ray analysis of the solid phase was conducted using a HZG 4/A-2 (Germany) diffractometer with continuous registration.

The criterion used for the X-ray analysis was based on the distribution curves of the dispersed radiation intensity $I = f(2\Theta)$. Wet crystals were analyzed directly after the equilibrium solution was filtered out. This procedure enabled a certain determination of the solid-phase composition being in equilibrium with the solutions.

Results and Discussion

Experimental results are tabulated in Table 1. The respective ion concentration values expressed in mole

Table 1. Solubility in the $NH_4Cl + NaVO_3 + NH_4VO_3 + NaCl + H_2O$ System at 303 K

	c/mol·dm^{-3}				mole fraction		
ρ/g·cm^{-3}	Cl^-	VO_3^-	NH_4^+	Na^+	$x_{NH_4^+}$	$x_{VO_3^-}$	solid phase
				E_1Q_1			
1.170	0.000	1.972	0.346	1.626	0.175	1.000	$NaVO_3$, NH_4VO_3
1.159	0.050	1.795	0.315	1.530	0.171	0.973	$NaVO_3$, NH_4VO_3
1.142	0.081	1.587	0.280	1.388	0.168	0.951	$NaVO_3$, NH_4VO_3
1.103	0.178	1.149	0.206	1.121	0.155	0.866	$NaVO_3$, NH_4VO_3
1.091	0.365	0.929	0.182	1.112	0.141	0.718	$NaVO_3$, NH_4VO_3
1.077	0.515	0.700	0.158	1.057	0.130	0.576	$NaVO_3$, NH_4VO_3
1.076	1.322	0.430	0.172	1.580	0.098	0.245	$NaVO_3$, NH_4VO_3
1.086	2.043	0.215	0.185	2.073	0.082	9.52×10^{-2}	$NaVO_3$, NH_4VO_3
1.110	2.942	5.33×10^{-2}	0.219	2.777	0.073	1.78×10^{-2}	$NaVO_3$, NH_4VO_3
1.128	3.720	2.44×10^{-2}	0.265	3.479	0.071	6.52×10^{-3}	$NaVO_3$, NH_4VO_3
1.164	4.714	6.49×10^{-3}	0.327	4.393	0.069	1.37×10^{-3}	$NaVO_3$, NH_4VO_3
1.192	5.577	1.51×10^{-3}	0.380	5.199	0.068	2.71×10^{-4}	$NaVO_3$, NH_4VO_3, NaCl
				E_2Q_1			
1.196	5.424	1.76×10^{-3}	0.000	5.426	0.000	3.24×10^{-4}	$NaVO_3$, NaCl
1.194	5.506	1.68×10^{-3}	0.154	5.354	0.026	3.05×10^{-4}	$NaVO_3$, NaCl
1.193	5.532	1.60×10^{-3}	0.272	5.262	0.049	2.89×10^{-4}	$NaVO_3$, NaCl
1.192	5.577	1.51×10^{-3}	0.380	5.199	0.068	2.71×10^{-4}	$NaVO_3$, NH_4VO_3, NaCl
				E_3Q_2			
1.170	7.021	0.000	3.720	3.301	0.530	0.000	NH_4Cl, NaCl
1.171	7.088	2.27×10^{-4}	3.831	3.257	0.540	3.21×10^{-5}	NH_4Cl, NH_4VO_3, NaCl
				E_4Q_2			
1.078	5.903	6.80×10^{-5}	5.904	0.000	1.000	1.15×10^{-5}	NH_4Cl, NH_4VO_3
1.085	6.012	1.01×10^{-4}	5.741	0.271	0.955	1.68×10^{-5}	NH_4Cl, NH_4VO_3
1.113	6.354	1.48×10^{-4}	5.112	1.242	0.805	2.33×10^{-5}	NH_4Cl, NH_4VO_3
1.135	6.567	1.84×10^{-4}	4.640	1.927	0.706	2.80×10^{-5}	NH_4Cl, NH_4VO_3
1.143	6.716	1.97×10^{-4}	4.452	2.264	0.663	2.94×10^{-5}	NH_4Cl, NH_4VO_3
1.167	7.102	2.22×10^{-4}	3.930	3.172	0.553	3.13×10^{-5}	NH_4Cl, NH_4VO_3
1.171	7.088	2.27×10^{-4}	3.831	3.257	0.540	3.21×10^{-5}	NH_4Cl, NH_4VO_3, NaCl
				Q_1Q_2			
1.192	5.577	1.51×10^{-3}	0.380	5.199	0.068	2.71×10^{-4}	$NaVO_3$, NH_4VO_3, NaCl
1.191	5.710	1.20×10^{-3}	0.439	5.272	0.077	2.10×10^{-4}	NH_4VO_3, NaCl
1.189	5.754	9.53×10^{-4}	0.550	5.205	0.096	1.66×10^{-4}	NH_4VO_3, NaCl
1.188	5.791	7.25×10^{-4}	0.798	4.994	0.138	1.25×10^{-4}	NH_4VO_3, NaCl
1.187	5.850	5.32×10^{-4}	1.030	4.821	0.176	9.10×10^{-5}	NH_4VO_3, NaCl
1.185	5.896	4.55×10^{-4}	1.223	4.673	0.207	7.72×10^{-5}	NH_4VO_3, NaCl
1.183	5.916	3.78×10^{-4}	1.480	4.436	0.250	6.39×10^{-5}	NH_4VO_3, NaCl
1.182	6.021	3.27×10^{-4}	1.671	4.350	0.277	5.43×10^{-5}	NH_4VO_3, NaCl
1.179	6.280	2.92×10^{-4}	2.248	4.032	0.358	4.65×10^{-5}	NH_4VO_3, NaCl
1.176	6.440	2.74×10^{-4}	2.682	3.758	0.416	4.25×10^{-5}	NH_4VO_3, NaCl
1.173	6.650	2.61×10^{-4}	3.110	3.540	0.468	3.92×10^{-5}	NH_4VO_3, NaCl
1.171	7.088	2.27×10^{-4}	3.831	3.257	0.540	3.21×10^{-5}	NH_4Cl, NH_4VO_3, NaCl

fractions according to the defined correlations:

$$x_{NH_4^+} = \frac{[NH_4^+]}{[NH_4^+] + [Na^+]} \quad \text{and} \quad x_{VO_3^-} = \frac{[VO_3^-]}{[VO_3^-] + [Cl^-]}$$

gave grounds for the construction of the solubility isotherm diagram in the title system (Figure 1). Thus, for this particular case, it was impossible to plot each of the experimental points listed in Table 1 on one figure, because the mole fraction values of vanadium salts change over an extensive range. Some points were neglected without compromising the figure's legibility as the isotherm branch course E_1Q_1 is rectilinear.

The course of the solubility isotherm system is markedly similar to that of the classical sodium system[1] $NaCl + NH_4HCO_3 + NaHCO_3 + NH_4Cl + H_2O$. Analogically, the respective crystallization areas are separated with five branches and two specific triple points. Only the size ratio of the crystallization areas for the particular salts is different and can be expressed approximately as 90000:10000:6:1 (NH_4VO_3:$NaVO_3$:NaCl:NH_4Cl). Crystallization area is a region limited by the respective coordinate axes and isotherm branches (Figure 1).

The largest crystallization region is that of ammonium vanadate (exceeding 90% of the whole diagram size), and particularly to be noted is that this is a salt of the lowest solubility. Therefore, most vanadium ions introduced into the after-filtration liquor are precipitated out and only insignificantly contaminate brine which is designated for the recarbonization process.

An X-ray analysis of the existing solid phase revealed clearly that only the initial salts exist in the system, i.e., NH_4VO_3, $NaVO_3$, NaCl, and NH_4Cl. No hydrates or binary salts appear at 303 K. Sodium chloride and ammonium vanadate are both chemically stable pair of salts, as the crystallization regions of these two salts are adjacent (Figure 1). This effect is of major importance for the proposed utilization as the reaction equilibrium (eq 3) is markedly shifted to the side of products, i.e., NH_4VO_3 and NaCl. The isotherm branch Q_1Q_2, which separates the crystallization regions of the stable pair of salts, is limited by two triple points Q_1 and Q_2, respectively. The locus of point Q_1 is represented by solutions inconvergently saturated; i.e., the salt compositions existing in the solid phase and in solution are different. The solid phase is composed of NH_4VO_3, $NaVO_3$, and NaCl, whereas in solution NH_4VO_3, NaCl, and NH_4Cl salts exist.

The other triple point Q_2 is represented by solutions convergently saturated; i.e., the salt composition detected in solution and in the solid phase remains the same, NH_4VO_3, NaCl, and NH_4Cl.

On the basis of the experimental data, it was concluded that the after-filtration liquor obtained from the Solvay method can be utilized and processed into ammonium vanadate.

Future research should be focused on the elimination of the unfriendly and laborious ammonium regeneration step using $Ca(OH)_2$ and the total utilization of sodium chloride employing the closed cycle process.

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