492 *J. Chem. Eng. Data* **2000,** *45,* 492−495

Solubility in the System $NaVO_3 + NH_4VO_3 + NH_3 + H_2O$ from 293 K to 323 K

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The solubility of $NaVO_3$ in aqueous ammonia solutions and the saturated solution densities have been determined between 293 K and 323 K. The data presented herein are essential for the assessment of optimum operating conditions for the production process of sodium carbonate introducing the modified Solvay method.

Introduction

$NaVO_3$ can be generated from NaCl and V_2O_5 in the presence of steam or oxygen:

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

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

Solutions of $NaVO_3$ in aqueous ammonia can undergo carbonization

$$NaVO_3 + NH_3 + CO_2 + H_2O \leftrightarrow NH_4VO_3(s) + NaHCO_3 \quad (3)$$

to form slightly soluble NH_4VO_3 (solubility of 0.05 $mol \cdot dm^{-3}$ at $T = 293$ K) and $NaHCO_3$, which remains in solution. This reaction sequence is used in industry to produce sodium hydrogen carbonate and is analogous to the traditional Solvay process (Niederliński et al., 1978) in which NaCl is used instead of $NaVO_3$ and $NaHCO_3$ is the salt with the lowest solubility (1.05 $mol \cdot dm^{-3}$ at $T = 293$ K).

Knowledge of the solubility in the $NaVO_3$ + ammonia + water system is essential for the preparation of vanadate-saturated ammonia solutions in the $NaVO_3$-based method. Also required, if the method is to be economically efficient, is detailed knowledge of the solubility isotherm for the reciprocal salt system Na^+, NH_4^+//HCO_3^-, VO_3^-, H_2O at $T = 303$ K (Wiktorow, 1975).

The solubility isotherm for the reciprocal salt system Na^+, NH_4^+//HCO_3^-, VO_3^-, H_2O is commonly represented in cited literature as a projection on a plane in Jänecke (ionic mole fraction) coordinates. Equilibrium data for three of the three-component systems that arise in this reciprocal system have been published by Trypuć and Kiełkowska (1995, 1996, 1997, 1998).

The experimental investigations to determine the exact position of lines separating the fields of salt cocrystallization located inside the diagram have been carried out, and the results and conclusions will soon be presented.

Since the literature inspection has not revealed any solubility data describing the title system, the equilibrium studies have been undertaken to present a comprehensive and reliable report.

The NH_3 concentration range and temperature of processing have been chosen on the basis of the operating parameters characterized in Solvay's method (Niederliński et al., 1978) and listed also in a previous paper by the authors (Trypuć and Białowicz, 1997). The interpretation of the $NaVO_3$ solubility data can be evaluated when the ongoing reaction between $NaVO_3$ and the aqueous ammonia solution (Trypuć and Białowicz, 1997), in the course of which NH_4VO_3 precipitates, is taken into account. The quantity of generated NH_4VO_3 is strictly limited by the initial NH_3 concentration introduced into solution and by the temperature.

Experimental Part

The solubility investigations of $NaVO_3$ in water + ammonia have been carried out within the range of NH_3 concentrations from 1 $mol \cdot dm^{-3}$ to 6 $mol \cdot dm^{-3}$. The temperature was fixed at four specific points: 293 K, 303 K, 313 K, and 323 K.

The $NaVO_3$ solubility in water + ammonia was determined employing the method of isothermal solution saturation.

In six water + ammonia solutions, the total NH_3 concentration increased in increments of about 1 $mol \cdot dm^{-3}$. The storage procedure for all solutions was designed to ensure a practically constant NH_3 concentration (Trypuć and Białowicz, 1997).

Analytical purity grade chemicals were applied for all of the experiments: $NaVO_3$ (>99% Merck) and NH_3 (Nitrogen Works Tarnów-Mościce SA, Poland).

Erlenmeyer flasks, each of 100 cm^3 volume, containing the projected excess of the solid phase and the projected concentration of water + ammonia solution, were closed with rubber stoppers and placed in a thermostated bath. Especially with higher NH_3 concentrations, at $T = 313$ K and $T = 323$ K, flasks were equipped with special metal holders to guarantee the proper closure procedure.

Preliminary tests showed that a specific reaction takes place in the system with precipitation of NH_4VO_3. For each initial water + ammonia solution, a constant volume of 50 cm^3 was designed to provide repeatability of the measurements and consistency for data interpretation.

The time of thermostating the particular samples was set up to 96 h, with continuous stirring to gain the state of complete equilibrium between the solution and the solid

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10.1021/je9901942 CCC: $19.00

phases at the given temperature. Temperature control was performed using a mercury thermometer with a precision of ±0.1 K.

After a fixed time limit, stirring was discontinued and the solids were sedimented. The time of clarification was about 24 h and depended upon the generated amount of NH_4VO_3 precipitates. Next, the clear solution was transferred to an Oswald pycnometer calibrated formerly over the temperature range between 293 K and 323 K. The total content of the pycnometer was used for the density determinations. The uncertainty of the density values was ± 0.002 g·cm^{-3}. Then the solution was transferred quantitatively to a graduated flask and the chemical analysis was carried out.

The sodium ion concentration was evaluated using the Kolthoff and Barbera balance method in the form of sodium zinc uranyl acetate (Furman, 1962) with a precision of measurements better than 1%.

The concentration of VO_3^- ions was examined employing the manganometric method, in the presence of H_2SO_4, after the reduction of vanadium ions with Fe(II) (Williams, 1985). The average relative error of the determination was <1%.

It should be noted that at $T = 293$ K with NH_3 concentrations of 5 and 6 mol·dm^{-3}, respectively, in water + ammonia solution after 48 h of thermostating, a reaction was detected. Undissolved sodium metavanadate and the unexpectedly great amount of generated NH_4VO_3 solids have taken up the total volume of the reaction flask. The insufficient quantity of the liquid phase made it impossible to perform an equilibrium solution analysis. The same conditions remained even with a longer duration of thermostating. Therefore, only four separate samples were measured, over the range of NH_3 concentrations from 1 mol·dm^{-3} to 4 mol·dm^{-3}.

The initial concentrations of the water + ammonia solutions were explored using the distillation method (Struszyński, 1982). The fully automatic distillation set was used [VAPODEST 30, Gerhardt]. NH_3 being removed in the isolated system (with the use of a strong base solution) was absorbed into the adjusted volume of the test acid solution. The residual excess of an acid was then potentiometrically titrated with a test NaOH solution. The precision of the measurements was estimated to be within 1%.

The identification of the solid phases in equilibrium with the solution phase was carried out by the X-ray method for all chosen points in the given range of temperatures. Therefore, after the equilibrium solution sampling, the solids were separated out from the solution using a glass crucible equipped with a sinter and a water aspirator. Next, prompt X-ray analysis was performed and, after a 24 h interval, repeated. The selected precipitate was stored in a desiccator at room temperature. The qualitative analysis of the precipitates was performed on an X-ray diffractometer (HZG-4/A-2, Germany), continuously registrated. The X-ray analyses of the solid phases were based on the distribution curves of the dispersed radiation intensity $I = f(\theta)$. For each separate diffraction pattern the interplanar distance (d) and the relative intensity (I) were given and then the comparison with data listed in the *Powder Diffraction File* (1976) was interpreted.

Results and Discussion

The $NaVO_3$ solubility data in water + ammonia derived from the chemical analysis of the equilibrium solutions are included in Table 1. The temperature of the measurements is expressed in K, the solution density is expressed in g·cm^{-3}, the component concentration of each system is expressed in mol·dm^{-3}, and the solid-phase composition is also given in the respective columns.

Table 1. Solubility of $NaVO_3$ in Water + Ammonia

ρ/g·cm^{-3}		c/mol·dm^{-3}				
NH_3 init	equil solut	NH_3 init	Na^+	VO_3^-	$Na^+ - VO_3^-$	solid phase
			$T = 293$ K			
	1.124	0.00	1.39	1.39	0.00	$NaVO_3 \cdot 2H_2O$
0.990	1.257	1.10	3.11	2.52	0.59	NH_4VO_3, $NaVO_3 \cdot 2H_2O$
0.983	1.389	1.98	4.92	3.63	1.29	NH_4VO_3, $NaVO_3 \cdot 2H_2O$
0.977	1.486	2.95	6.57	4.54	2.03	NH_4VO_3, $NaVO_3 \cdot 2H_2O$
0.970	1.536	3.89	7.22	4.88	2.34	NH_4VO_3, $NaVO_3 \cdot 2H_2O$
			$T = 303$ K			
	1.138	0.00	1.61	1.61	0.00	$NaVO_3 \cdot 2H_2O$
0.990	1.299	1.10	3.52	3.07	0.45	NH_4VO_3, $NaVO_3 \cdot 2H_2O$
0.983	1.388	1.98	4.88	3.86	1.02	NH_4VO_3, $NaVO_3 \cdot 2H_2O$
0.977	1.454	2.95	5.92	4.37	1.55	NH_4VO_3, $NaVO_3 \cdot 2H_2O$
0.970	1.503	3.89	6.60	4.91	1.69	NH_4VO_3, $NaVO_3 \cdot 2H_2O$
0.963	1.527	4.87	7.00	5.12	1.88	NH_4VO_3, $NaVO_3 \cdot 2H_2O$
0.953	1.535	6.25	7.20	5.36	1.84	NH_4VO_3, $NaVO_3 \cdot 2H_2O$
			$T = 313$ K			
	1.151	0.00	1.82	1.82	0.00	$NaVO_3 \cdot 2H_2O$
0.990	1.322	1.09	3.70	3.38	0.32	NH_4VO_3, $NaVO_3 \cdot 2H_2O$
0.983	1.383	1.97	4.64	3.92	0.72	NH_4VO_3, $NaVO_3 \cdot 2H_2O$
0.977	1.431	2.93	5.46	4.32	1.14	NH_4VO_3, $NaVO_3 \cdot 2H_2O$
0.970	1.468	3.85	5.93	4.68	1.25	NH_4VO_3, $NaVO_3 \cdot 2H_2O$
0.963	1.489	4.87	6.22	4.88	1.34	NH_4VO_3, $NaVO_3 \cdot 2H_2O$
0.954	1.498	6.19	6.39	5.03	1.36	NH_4VO_3, $NaVO_3 \cdot 2H_2O$
			$T = 323$ K			
	1.179	0.00	2.09	2.09	0.00	$NaVO_3 \cdot 2H_2O$
0.990	1.325	1.09	3.73	3.55	0.18	NH_4VO_3, $NaVO_3 \cdot 2H_2O$
0.983	1.374	1.97	4.44	3.97	0.47	NH_4VO_3, $NaVO_3 \cdot 2H_2O$
0.977	1.404	2.93	4.88	4.21	0.67	NH_4VO_3, $NaVO_3 \cdot 2H_2O$
0.970	1.432	3.85	5.21	4.44	0.77	NH_4VO_3, $NaVO_3 \cdot 2H_2O$
0.963	1.443	4.87	5.42	4.54	0.88	NH_4VO_3, $NaVO_3 \cdot 2H_2O$
0.954	1.450	6.19	5.60	4.62	0.98	NH_4VO_3, $NaVO_3 \cdot 2H_2O$

Solubility data of $NaVO_3$ in water versus temperature are also listed in Table 1 (Trypuć and Kiełkowska, 1997).

Each randomized value presented in Table 1 was determined as the arithmetical average of results obtained from the analysis of three simultaneously prepared equilibrium solutions. The average relative error was calculated to be within ±0.5%.

The following reaction is consistent with the experimental data:

$$NaVO_3 + NH_3 + H_2O \leftrightarrow NH_4VO_3(s) + NaOH \qquad (4)$$

where the VO_3^- ions introduced into solution as a sodium vanadate salt partially precipitate as NH_4VO_3. According to the observed double-displacement reaction, the $NaVO_3$ solubility values increase proportionally to the generated quantity of NH_4VO_3 solids.

As long as $NaVO_3$ is the only solid in equilibrium with the liquid phase, $[Na^+] = [VO_3^-]$ and the system is ternary. When NH_4VO_3 precipitates as well, the ternary system becomes the quaternary system $NaVO_3 + NH_4VO_3 + NH_3 + H_2O$ and can be considered to contain, in the solution phase, six species: Na^+, NH_4^+, VO_3^-, OH^-, NH_3, and H_2O. There are two constraints on the concentrations of these species: the ionization equilibrium of aqueous ammonia and the charge balance:

$$[Na^+] + [NH_4^+] = [VO_3^-] + [OH^-] \qquad (5)$$

leaving four independent solute concentrations.

Because of the small ionization constant of aqueous ammonia and the large ammonia and hydroxide ion concentrations when ammonium vanadate precipitates, the

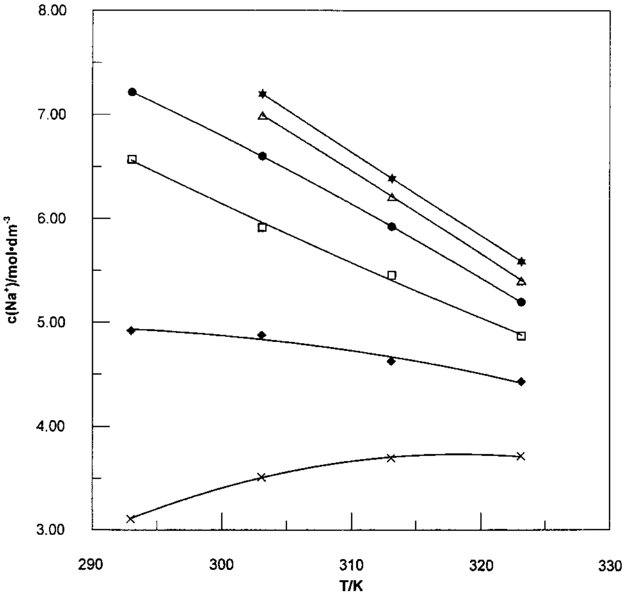

Figure 1. Na^+ ion concentration dependence on temperature, for the constant NH_3 concentrations: ×, $c_{NH_3} = 1.1$ mol·dm^{-3}; ◆, $c_{NH_3} = 2.0$ mol·dm^{-3}; □, $c_{NH_3} = 2.9$ mol·dm^{-3}; ●, $c_{NH_3} = 3.9$ mol·dm^{-3}; △, $c_{NH_3} = 4.9$ mol·dm^{-3}; ★, $c_{NH_3} = 6.2$ mol·dm^{-3}.

concentration of ammonium ion is negligible in the charge balance equation. The hydroxide ion concentration in Table 1 is then given by

$$[OH^-] = [Na^+] - [VO_3^-] \tag{6}$$

Analyses for Na^+, VO_3^-, and NH_3 are necessary to characterize the system. If it assumed that there is no change in volume on adding salt to the ammonia solution, material balance equations for Na^+, VO_3^-, and NH_3 give

$$[NH_3] = [NH_3]_T - [Na^+] + [VO_3^-] \tag{7}$$

where the subscript T indicates the initial concentration before addition of salt. Thus, the ammonia concentration in the solution at equilibrium can be calculated approximately from the initial concentration.

The determined sodium ion concentration is represented as an overall quantity of dissolved $NaVO_3$. It seems apparent that sodium ions found in water + ammonia solutions are exclusively derived from dissolution of $NaVO_3$, and therefore, the $NaVO_3$ solubility in aqueous ammonia solutions can be interpreted as the total sodium ions concentration.

According to the data summarized in Table 1, the initial concentrations of the aqueous ammonia solutions change only insignificantly and for that reason can be acknowledged as constant.

Figure 1 presents the dependence of the Na^+ ion concentration as a function of temperature for the constant NH_3 concentration applied.

The course of particular curves in Figure 1 shows that with increasing NH_3 concentration the Na^+ ion concentration also becomes greater for each experimental temperature. The observed increment becomes smaller with the increase in temperature values.

On the basis of data collected in Table 1, the temperature influence on the $NaVO_3$ solubility in water + ammonia with a constant NH_3 concentration has been recognized. The solubility increases only when the specific NH_3 concentration equal to 1 mol·dm^{-3} was introduced. Over the NH_3 concentration range 2−6 mol·dm^{-3}, the $NaVO_3$ solubility decreases systematically with the rise in temperature values.

The comparison of solubility data for the $NaVO_3$ salt in aqueous ammonia solutions and pure water at corresponding temperatures points out that the NH_3 presence in solution causes a significant increase in the solubility values for $NaVO_3$. The detected effect is economically profitable with regard to the discussed vanadium method of industrial production of sodium hydrogen carbonate.

On the basis of compiled experimental data, the calculated difference between the concentrations of sodium and vanadium ions for the adequate equilibrium solutions is presented in Table 1. In the column entitled ($Na^+ - VO_3^-$) the exact quantities of VO_3^- ions precipitated as NH_4VO_3 as a consequence of the detected reaction are given. The conversion degree of $NaVO_3$ into NH_4VO_3 can be presented with the following ion concentration proportion: $[Na^+ - VO_3^-]/[Na^+]$. Data analysis (Table 1) points out that the $NaVO_3$ conversion degree increases with the rise in NH_3 concentration values for the given temperature whereas it decreases with the increase of temperature for constant NH_3 concentrations. This fact suggests an exothermic character of the detected reaction in the system.

X-ray analysis of the solid phase revealed that, in the case of all the samples employed in experiments, the precipitate in equilibrium with the mother liquor (the solution in equilibrium with the solid phase) was the mixture of NH_4VO_3 and $NaVO_3$ salts.

The solid-phase analysis performed directly after separation from the mother liquor demonstrated that $NaVO_3$ exists only in a hydrated form: $NaVO_3{\cdot}2H_2O$. Analysis after a 24 h interval revealed an additional appearance of the β-$NaVO_3$ isomer. For the longer duration the quantitative distribution of the detected new solid phases changed with the increase in β-$NaVO_3$ formation. Obviously, the hydrated forms of $NaVO_3$ are chemically unstable, water molecules being only weakly bonded to the crystal structure, and even at room temperature and in a dry environment can transform into the isomer form of β-$NaVO_3$. The complete transformation of hydrates into β-$NaVO_3$ was observed at the temperature 307 K, which can also be found in recent literature (Kuok et al., 1995).

This fact confirms the ongoing reaction, in the course of which NH_4VO_3 is precipitated. The detected effect is quite unusual in the case of the investigated solubility of many inorganic salts in water + ammonia, for example, $NaCl + NH_3 + H_2O$ (Trypuć, 1987), $KCl + NH_3 + H_2O$ (Koneczny et al., 1973), $KNO_3 + NH_3 + H_2O$ (Lango, 1971).

The rate of formation of NH_4VO_3 solids as compared to $NaVO_3$ is strictly limited to the initial NH_3 concentration applied and the temperature. Unfortunately, further determinations of $NaVO_3$ forms found in the solid phase and also their solubilities in water + ammonia seem still unresolved and need further research.

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Received for review July 17, 1999. Accepted February 9, 2000.

JE9901942