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# Articles

## Solubility in the $NH_4HCO_3 + NH_4VO_3 + H_2O$ System

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The solubility of ammonium bicarbonate and ammonium vanadate in the $NH_4HCO_3 + NH_4VO_3 + H_2O$ system has been investigated at 293 K to 323 K. A polytherm section of the system has been drawn. The change of mutual salt concentrations and the density of the solutions as a function of the temperature have been described by the appropriate equations. The equations can be used for the detailed calculations of the $NH_4HCO_3$ concentration and the density of the solutions for any temperature within the investigated range.

### Introduction

There have been studies on the method of simultaneous production of soda and hydrochloric acid or chlorine based on NaCl and the intermediate reactant $V_2O_5$ in the presence of steam or oxygen (U.S. patent, 1967). Chemical reactions presented in patent-67 do not give any information about the kinetics of carbonation and crystallization processes of $NH_4VO_3$ or the determination of the composition of the solutions subject to carbonation.

Trypuć and Kiełkowska (1995) presented the results of the equilibrium in the $NaVO_3 + NaHCO_3 + H_2O$ system. These results are useful for obtaining isotherms of the reciprocal salt pairs system $NaVO_3 + NH_4HCO_3 + H_2O$ in the oblique projection according to Janecki (Wiktorow, 1975). Such diagrams are necessary to determine the optimum conditions for carrying out the modified soda production process based on the Solvay method. The ternary system is represented by one side of the equilibrium diagram square. The rest of the sides represent the following systems: $NH_4HCO_3 + NH_4VO_3 + H_2O$, $NaVO_3 + NH_4VO_3 + H_2O$, and $NaHCO_3 + NH_4HCO_3 + H_2O$. This last system has been studied previously (Pelsh, 1969).

This paper deals with the $NH_4HCO_3 + NH_4VO_3 + H_2O$ system. Equilibrium studies were made in the temperature range 293 K to 323 K. This planned research in the given range of temperatures was caused mainly by two important factors: the decomposition temperature of $NH_4HCO_3$ (ca. 333 K) (Niederliński et al., 1978) and the highest maximal temperature attainable in the carbonating columns in Solvay's method of producing soda (Szokin and Kraszeninnikow, 1975).

### Experimental Section

The investigations on the solubility of ammonium bicarbonate and ammonium vanadate in water were carried out in the temperature range 293 K to 323 K. The determination of the solubility isotherms of the $NH_4HCO_3 + NH_4VO_3 + H_2O$ system required conducting many equilibrium investigations.

Analytical grade salts $NH_4HCO_3$ (POCh Gliwice, Poland) and $NH_4VO_3$ (Aldrich Chemical Co. Ltd.) were used.

The apparatus has been described previously by Koneczny *et al.* (1978) and Trypuć (1980). The effect of pressure at 313 K and 323 K was given by Trypuć (1974). Erlenmeyer flasks, each 100 cm$^3$ capacity, containing suitable amounts of salt and distilled water, were closed with stoppers and placed in the thermostat for both temperatures 293 K and 303 K.

For both temperatures 313 K and 323 K the precise measurements were taken in the reaction flask closed with a rubber stopper, with two glass tubes in it. One of them was closed by a funnel for pouring in water, while the other served for obtaining a vacuum, letting in $CO_2$, and sequential sampling. The reaction flask was linked with a U-tube manometer, filled with mercury, in order to measure the actual pressure with an accuracy of ±0.5 mm.

To achieve higher levels of solution carbonation ($R >$ 90%) at 313 K and 323 K, additional gaseous $CO_2$ at pressures up to 2.5 bar to 3.0 bar was added. It was a guarantee to find both in the solution and in the precipitate only $NH_4HCO_3$ salt and not the binary mixture of $NH_4HCO_3$ and $(NH_4)_2CO_3$.

The time of thermostating the individual samples was 72 h, while the samples were being constantly stirred. This ensured equilibrium between the solution and the solid phase at the given temperature. The temperatures were measured with an accuracy of ±0.1 deg.

After the set time limit stirring was stopped in order to decant the solid phase. The clear solution was sampled to the calibrated, at the given temperature, Ostwald pycnometer. The use of this pycnometer was necessary to measure the density of the systems with higher pressures. The total content of the pycnometer served for determination of $VO_3^-$ and $NH_4^+$ ion concentrations.

The concentration of $VO_3^-$ ions was determined by the manganometric method after reduction with iron(II) (Struszyński, 1954; Williams, 1985). The concentration of $NH_4^+$ ions was determined by the distillation method with the addition of Devard's alloy, which protected $NH_3$ from being oxidized to $N_2$ under the influence of $VO_3^-$ ions (Struszyński, 1954; Williams, 1985).

The identification of the solid phases in equilibrium solution was performed by analytical and X-ray methods. The qualitative analyses were carried out on an X-ray diffractometer (HZG-4/A-2; GDR) with continuous registration. The X-ray analysis of the solid phases were based on the distribution curves of the dispersed radiation intensity $I = f(\theta)$.

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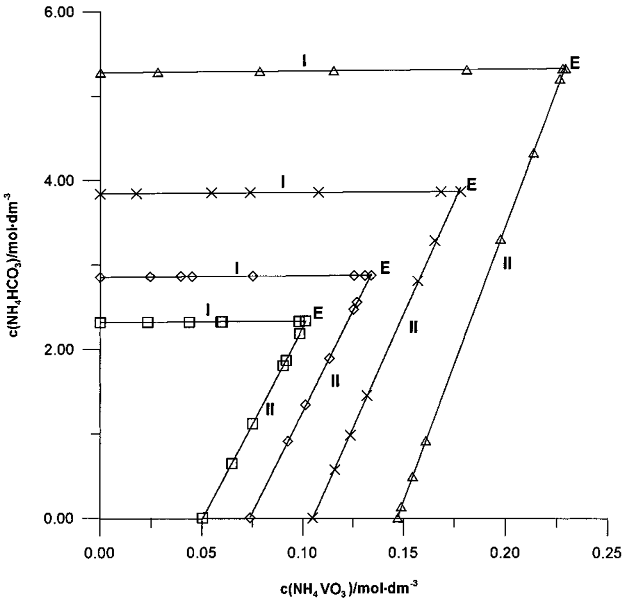

**Figure 1.** Solubility of $NH_4HCO_3$ and $NH_4VO_3$ in the $NH_4HCO_3 + NH_4VO_3 + H_2O$ system: (□) $T = 293$ K; (◇) $T = 303$ K; (×) $T = 313$ K; (△) $T = 323$ K.

## Results and Discussion

Branches I (Figure 1) of the solubility isotherms correspond to solutions saturated with $NH_4HCO_3$ with increasing concentrations of $NH_4VO_3$ toward the eutonic points.

Branches II (Figure 1) correspond to solubility isotherms where the solution was saturated with $NH_4VO_3$ and the concentration of $NH_4HCO_3$ was increasing toward the eutonic points.

The eutonic points E correspond to the solutions saturated with both $NH_4HCO_3$ and $NH_4VO_3$.

The solubility of ammonium bicarbonate and ammonium vanadate in water is presented in Table 1. Figure 1 shows a polytherm of the $NH_4HCO_3 + NH_4VO_3 + H_2O$ system. The dependence of solution density on the concentration of $NH_4VO_3$ is shown in Figure 2.

The salt concentration and the density of the solutions on the individual branches of the solubility isotherms, as well as the temperature dependence, have been described with appropriate mathematical equations.

As can be seen from Table 1, the concentration of ammonium bicarbonate changes slightly with the increase in the ammonium vanadate concentration (branch I). Consequently, this slight dependence has been introduced to the equation for the temperature dependence which shows the overall relation given by the equation

$$c(\mathrm{NH_4HCO_3})/\mathrm{mol{\cdot}dm^{-3}} = Ac(\mathrm{NH_4VO_3})/\mathrm{mol{\cdot}dm^{-3}} + B_1(T/\mathrm{K})^2 + B_2(T/\mathrm{K}) + B_3 \quad (1)$$

The change of ammonium vanadate concentration in the eutonic points, depending on temperature, is presented by the equation

$$c_\mathrm{E}(\mathrm{NH_4VO_3})/\mathrm{mol{\cdot}dm^{-3}} = B(\mathrm{T/K})^2 + B_2(T/\mathrm{K}) + B_3 \quad (2)$$

The influence of temperature on the $NH_4VO_3$ solubility in water is given by the equation

$$c(\mathrm{NH_4VO_3})/\mathrm{mol{\cdot}dm^{-3}} = B_1(T/\mathrm{K})^2 + B_2(T/\mathrm{K}) + B_3 \quad (3)$$

**Table 1. Solubility in the System $NH_4HCO_3 + NH_4VO_3 + H_2O$**

| | g·cm⁻³ | | c/mol·dm⁻³ | | | |
|---|---|---|---|---|---|---|
| T/K | ρ | ρ(calc) | $NH_4VO_3$ | $NH_4HCO_3$ | $NH_4HCO_3$ (calc) | composition of the solid phase |
| 293 | 1.072 | 1.072 | 0 | 2.317 | 2.312 | $NH_4HCO_3$ |
| | 1.073 | 1.073 | 0.0232 | 2.318 | 2.314 | $NH_4HCO_3$ |
| | 1.074 | 1.073 | 0.0436 | 2.319 | 2.315 | $NH_4HCO_3$ |
| | 1.074 | 1.074 | 0.0593 | 2.321 | 2.317 | $NH_4HCO_3$ |
| | 1.074 | 1.074 | 0.0601 | 2.322 | 2.317 | $NH_4HCO_3$ |
| | 1.076 | 1.076 | 0.0981 | 2.325 | 2.320 | $NH_4HCO_3$ |
| | 1.076 | 1.079 | 0.1012 | 2.331 | 2.320 | $NH_4HCO_3$, $NH_4VO_3$ |
| | 1.072 | 1.079 | 0.0984 | 2.180 | 2.174 | $NH_4VO_3$ |
| | 1.062 | 1.069 | 0.0916 | 1.865 | 1.864 | $NH_4VO_3$ |
| | 1.060 | 1.067 | 0.0901 | 1.800 | 1.796 | $NH_4VO_3$ |
| | 1.037 | 1.045 | 0.0751 | 1.117 | 1.109 | $NH_4VO_3$ |
| | 1.021 | 1.030 | 0.0647 | 0.642 | 0.640 | $NH_4VO_3$ |
| | 1.001 | 1.009 | 0.0503 | 0 | 0.015 | $NH_4VO_3$ |
| 303 | 1.094 | 1.094 | 0 | 2.854 | 2.862 | $NH_4HCO_3$ |
| | 1.094 | 1.095 | 0.0245 | 2.857 | 2.864 | $NH_4HCO_3$ |
| | 1.095 | 1.095 | 0.0395 | 2.859 | 2.865 | $NH_4HCO_3$ |
| | 1.096 | 1.095 | 0.0450 | 2.860 | 2.866 | $NH_4HCO_3$ |
| | 1.096 | 1.097 | 0.0750 | 2.864 | 2.868 | $NH_4HCO_3$ |
| | 1.098 | 1.099 | 0.1254 | 2.871 | 2.872 | $NH_4HCO_3$ |
| | 1.098 | 1.099 | 0.1308 | 2.872 | 2.872 | $NH_4HCO_3$ |
| | 1.099 | 1.094 | 0.1340 | 2.872 | 2.872 | $NH_4HCO_3$, $NH_4VO_3$ |
| | 1.086 | 1.078 | 0.1268 | 2.550 | 2.527 | $NH_4VO_3$ |
| | 1.083 | 1.075 | 0.1251 | 2.467 | 2.447 | $NH_4VO_3$ |
| | 1.062 | 1.057 | 0.1132 | 1.886 | 1.886 | $NH_4VO_3$ |
| | 1.044 | 1.038 | 0.1012 | 1.337 | 1.320 | $NH_4VO_3$ |
| | 1.027 | 1.024 | 0.0925 | 0.910 | 0.910 | $NH_4VO_3$ |
| | 1.002 | 0.994 | 0.0738 | 0 | 0.028 | $NH_4VO_3$ |
| 313 | 1.116 | 1.115 | 0 | 3.839 | 3.862 | $NH_4HCO_3$ |
| | 1.116 | 1.116 | 0.0177 | 3.843 | 3.864 | $NH_4HCO_3$ |
| | 1.118 | 1.118 | 0.0545 | 3.847 | 3.866 | $NH_4HCO_3$ |
| | 1.118 | 1.118 | 0.0736 | 3.851 | 3.868 | $NH_4HCO_3$ |
| | 1.120 | 1.120 | 0.1077 | 3.855 | 3.870 | $NH_4HCO_3$ |
| | 1.122 | 1.122 | 0.1683 | 3.857 | 3.875 | $NH_4HCO_3$ |
| | 1.122 | 1.118 | 0.1779 | 3.858 | 3.876 | $NH_4HCO_3$, $NH_4VO_3$ |
| | 1.099 | 1.093 | 0.1653 | 3.280 | 3.254 | $NH_4VO_3$ |
| | 1.091 | 1.079 | 0.1570 | 2.806 | 2.803 | $NH_4VO_3$ |
| | 1.044 | 1.037 | 0.1318 | 1.450 | 1.434 | $NH_4VO_3$ |
| | 1.031 | 1.024 | 0.1236 | 0.982 | 0.989 | $NH_4VO_3$ |
| | 1.018 | 1.011 | 0.1160 | 0.571 | 0.576 | $NH_4VO_3$ |
| | 1.002 | 0.993 | 0.1050 | 0 | 0.022 | $NH_4VO_3$ |
| 323 | 1.138 | 1.137 | 0 | 5.277 | 5.312 | $NH_4HCO_3$ |
| | 1.138 | 1.138 | 0.0281 | 5.281 | 5.314 | $NH_4HCO_3$ |
| | 1.139 | 1.140 | 0.0783 | 5.288 | 5.318 | $NH_4HCO_3$ |
| | 1.139 | 1.142 | 0.1152 | 5.294 | 5.321 | $NH_4HCO_3$ |
| | 1.140 | 1.145 | 0.1808 | 5.299 | 5.326 | $NH_4HCO_3$ |
| | 1.141 | 1.146 | 0.2276 | 5.312 | 5.329 | $NH_4HCO_3$ |
| | 1.142 | 1.145 | 0.2290 | 5.313 | 5.329 | $NH_4HCO_3$, $NH_4VO_3$ |
| | 1.136 | 1.140 | 0.2263 | 5.191 | 5.137 | $NH_4VO_3$ |
| | 1.116 | 1.119 | 0.2135 | 4.316 | 4.309 | $NH_4VO_5$ |
| | 1.087 | 1.092 | 0.1975 | 3.296 | 3.274 | $NH_4VO_3$ |
| | 1.027 | 1.031 | 0.1610 | 0.197 | 0.912 | $NH_4VO_3$ |
| | 1.016 | 1.202 | 0.1545 | 0.490 | 0.492 | $NH_4VO_3$ |
| | 1.005 | 1.011 | 0.1490 | 0.135 | 0.136 | $NH_4VO_3$ |
| | 1.003 | 1.008 | 0.1472 | 0 | 0.019 | $NH_4VO_3$ |

Equations 2 and 3 are necessary for determining the equilibrium concentrations of $NH_4HCO_3$ and $NH_4VO_3$ for branch II of the solubility isotherms limited by the eutonic points E and the solubility of $NH_4VO_3$ in water.

The temperature dependencies of the density and the saturated solutions of ammonium vanadate are also described by appropiate equations shown in Figure 2.

For branch I of the solubility isotherms (the crystallization area of $NH_4HCO_3$), the change of the solution density is given by the equation

$$\rho_\mathrm{I}/\mathrm{g{\cdot}cm^{-3}} = Ac(\mathrm{NH_4VO_3})/\mathrm{mol{\cdot}dm^{-3}} + B_2(T/\mathrm{K}) + B_3 \quad (4)$$

For branch II of the solubility isotherms (the crystallization area of $NH_4VO_3$), the changes of density are given by the equation

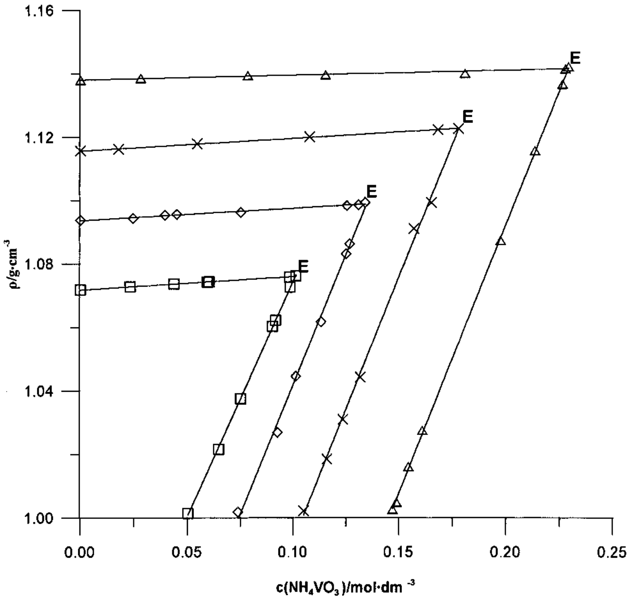

**Figure 2.** Density–concentration relationships of $NH_4VO_3$ in the $NH_4HCO_3 + NH_4VO_3 + H_2O$ system: (□) $T = 293$ K; (◇) T = 303 K; (×) $T = 313$ K; (△) $T = 323$ K.

$$\rho_{II}/\text{g}\cdot\text{cm}^{-3} = (B_1(T/\text{K})^2 + B_2(T/\text{K}) + B_3)c(NH_4VO_3)/\text{mol}\cdot\text{dm}^{-3} + C_1(T/\text{K}) + C_2 \quad (5)$$

The numerical values of the coefficients and the average relative error of the above given eqs 1–5 are shown in Table 2.

From Table 1 the equations for the solution density and saturated solutions of the salts are in good agreement with the experimental values.

The solubility isotherms (Figure 1) show that with the increase of $NH_4VO_3$ concentration (the crystallization area of $NH_4HCO_3$, branch I), the concentration of $NH_4HCO_3$ increases slightly toward the eutonic points.

The course of branch II of the respective isotherm shows that the concentration of $NH_4HCO_3$ decreases rapidly (beginning from the eutonic points) along with the slight changes of $NH_4VO_3$ concentration for a given temperature.

From Figure 1 the individual isotherms do not differ from each other; the shift being caused primarily by the changes of temperature. The solubility of $NH_4HCO_3$ and $NH_4VO_3$ increases with the increase of temperature.

The concentration of $NH_4HCO_3$ at $T = 323$ K is 127% higher than that at $T = 293$ K, whereas the solubility of $NH_4VO_3$ is 192% higher for the same conditions. Hence, the solubility of $NH_4VO_3$ depends more on temperature than on the solubility of $NH_4HCO_3$.

**Table 2. Coefficients and the Average Relative Error in Eqs 1–5**

| | values of the coefficients | | | | | | |
|---|---|---|---|---|---|---|---|
| eq | $A$ | $10^{-4} B_1$ | $10^{-2} B_2$ | $B_3$ | $10^{-3} C_1$ | $C_2$ | av rel error/% |
| 1 | 0.075 | 22.5 | −128.6 | −185.95 | | | 0.34 |
| 2 | | 0.49 | −2.592 | 3.489 | | | 0.26 |
| 3 | | 0.4675 | −2.558 | 3.5319 | | | 0.39 |
| 4 | 0.04 | | 0.219 | 0.43 | | | 0.07 |
| 5 | | −2.49 | 16.02 | −24.1 | −5.75 | 2.62 | 0.58 |

For saturated solutions of $NH_4HCO_3$, the densities of the solutions increase slightly with the increase in $NH_4VO_3$ concentration and reach a maximum at the eutonic points E. Having crossed the points, the densities decrease to the values of the densities of saturated solutions of $NH_4VO_3$ (Figure 2).

The crystallization area of the salt of the lowest solubility, $NH_4VO_3$, spreads out in the Janecki diagram of the reciprocal salt pairs system ($NaVO_3 + NH_4HCO_3 + H_2O$) over the largest area.

On the basis of the X-ray analysis of the precipitates and the monotonic course of the solubility isotherms, it can be concluded that a new solid phase is not created in this system (Sułajmankułov, 1971).

## Literature Cited

Koneczny, H.; Lango, D.; Lango, M. The investigations on KCl-$NH_3$-$H_2O$ system. *Chem. Stos.* **1978**, *22*, 115–125 (in Polish).

Niederliński, A.; Bukowski, A.; Koneczny, H. *Soda i produkty towarzyszące*; WNT: Warsaw, Poland, 1978.

Pelsh, A. D. *Spravotschnik po Rastvorimosti Solyevykh System, "Nauka"*; Goskhimisdat: Leningrad, Russia, 1969; Vol. III.

Struszyński, M. *Analiza ilościowa i techniczna*; PWT: Warsaw, Poland, 1954.

Sułajmankułov, K. *Sojedinienia karbamida s nieorganitscheskimi soliami*; ILIM: Frunze, Russia, 1971.

Szokin, I. N.; Kraszeninnikow, S. A. *Technologia sody*; Chimia: Moscow, Russia, 1975.

Trypuć, M. The equilibrium investigations of the systems: NaCl-$NH_3$-$CO_2$-$H_2O$, $NaNO_3$-$NH_3$-$CO_2$-$H_2O$, KCl-$NH_3$-$CO_2$-$H_2O$, $KNO_3$-$NH_3$-$CO_2$-$H_2O$, in the presence of urea, in the triple point $P_1$. *UMK Toruń* **1974** (in Polish).

Trypuć, M. The solubility investigations of NaCl in aqueous ammonia solution in the presence of urea. *Chem. Stos.* **1980**, *24*, 365–376 (in Polish).

Trypuć, M.; Kiełkowska, U. The investigation on $NaVO_3$-$NaHCO_3$-$H_2O$ system. *Pol. J. Appl. Chem.* **1995**, *1*, 103–109.

U.S. Patent 3.313.593, 1967.

Wiktorow, M. M. *Obliczenia graficzne w technologii substancji nieorganicznych*; WNT: Warsaw, Poland, 1975.

Williams, W. J. *Oznaczanie anionów*; PWN: Warsaw, Poland, 1985.

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