

# The Influence of Urea on the $\text{KHCO}_3$ and $\text{NH}_4\text{VO}_3$ Solubility in the $\text{KHCO}_3 + \text{NH}_4\text{VO}_3 + \text{H}_2\text{O}$ System

Urszula Kielkowska, Mieczysław Trypuć, Krzysztof Mazurek, Sebastian Drużyński

Nicolaus Copernicus University, Faculty of Chemistry, ul. Gagarina 7, 87-100 Toruń, Poland, tel. (+48 56) 611 45 36, fax (+48 56) 654 24 77, e-mail: ulak@chem.uni.torun.pl

The influence of urea on the vanadium(V) and potassium ion concentrations in the  $\text{KHCO}_3 + \text{NH}_4\text{VO}_3 + \text{H}_2\text{O}$  system was determined in the temperature range of 293 K to 303 K. Additionally, the solution density dependence versus the urea concentration was presented. These data are essential for the assessment of optimum operating conditions for the new production process of potassium carbonate.

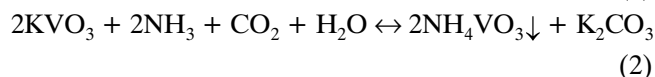
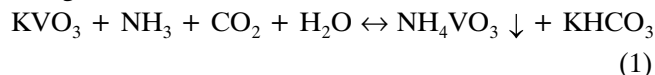
**Keywords:** solubility, density, equilibrium, ammonium metavanadate(V), potassium bicarbonate, urea.

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

## INTRODUCTION

The data presented herein is essential for the evaluation of a wasteless production method of potassium carbonate based on KCl and  $\text{V}_2\text{O}_5$  in the presence of steam or oxygen<sup>1-3</sup>.

A very important step of the vanadate method of  $\text{K}_2\text{CO}_3$  production is the process of the carbonization of a water + ammonia solution of  $\text{KVO}_3$ , consisting of polithermic-polibarc chemisorptions of carbon dioxide and crystallization of ammonium metavanadate(V)<sup>4-5</sup>. The efficiency of that process would determine the basic material and energetic indicators of the described method.



In both these processes,  $\text{NH}_4\text{VO}_3$  will precipitate and the solution will contain a mixture of  $\text{KHCO}_3$  and  $\text{K}_2\text{CO}_3$ . The ratio of their concentration would depend on the degree of the system's carbonization.

The cited literature reviews concerning the mutual solubility of urea and various inorganic salts in an aqueous solution are extensive<sup>6-8</sup>. In many ternary systems, urea is a component that forms compounds with the salt and which leads to a significant decrease or increase of the salts solubility.

Our research on the possibility of urea use to minimizing the losses of the vanadium(V) compounds in the process of  $\text{K}_2\text{CO}_3$  production is currently under study<sup>9</sup>. One of the possibility steps that urea might be used in, is the separation of residual  $\text{NH}_4\text{VO}_3$  out of the post-filtration liquor and subsequent evaporation to obtain pure  $\text{KHCO}_3$ . After the calcinations stage,  $\text{K}_2\text{CO}_3$  are generated.

The present paper is a continuation of the research on the influence of urea on the solubility of vanadium(V) compounds.

## EXPERIMENTAL

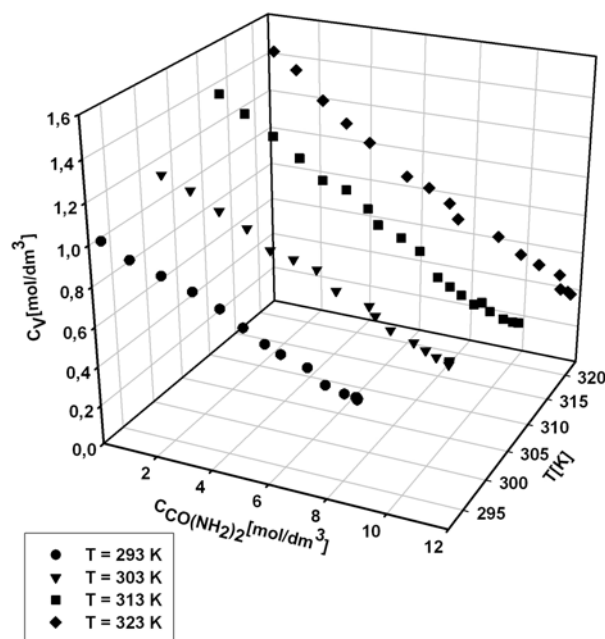
**Materials:** Analytical pure chemicals:  $\text{NH}_4\text{VO}_3$  (purity of 99%, Aldrich),  $\text{KHCO}_3$  (purity of 99.98%, POCh Gliwice S.A., Poland) and  $\text{CO}(\text{NH}_2)_2$  (purity of 99.5 %, POCh Gliwice S.A., Poland) were used for all experiments, without further purification.

POCh Gliwice S.A., Poland) were used for all experiments, without further purification.

**Experimental Procedure:** The influence of urea on the vanadium(V) and potassium ion concentrations in the system  $\text{KHCO}_3 + \text{NH}_4\text{VO}_3 + \text{H}_2\text{O}$  was determined in the temperature range of 293 – 323 K, using the isothermal solution saturation method. A Polystat CC1 thermorelay (Germany), with a precision of  $\pm 0.02$  K was used for temperature control.

A flask, containing a known amount of substances and 50 cm<sup>3</sup> of distilled water was placed in a thermostated bath. Each sample solution was stirred continuously for 120 hours to reach equilibrium between the solution and the solid phase.

After this time, stirring was stopped and the solutions were left for the solid phase to decant. The clear equilibrium solution was sampled into a calibrated Ostwald pycnometer. A detailed description of the sampling procedure has been described in former papers<sup>4, 10</sup>.



**Figure 1.** The vanadium(V) concentration dependence on the urea concentration at four different temperatures: 293 K, 303 K, 313 K, 323 K

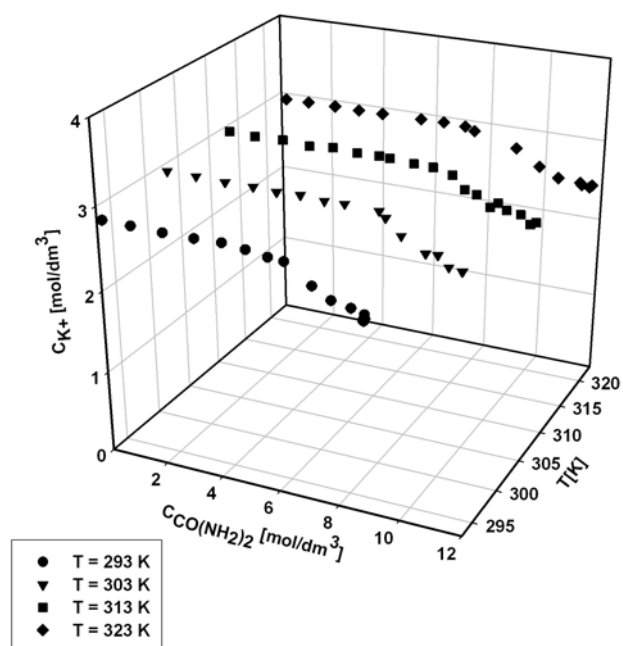


Figure 2. The potassium ions concentration dependence on the urea concentration and temperature

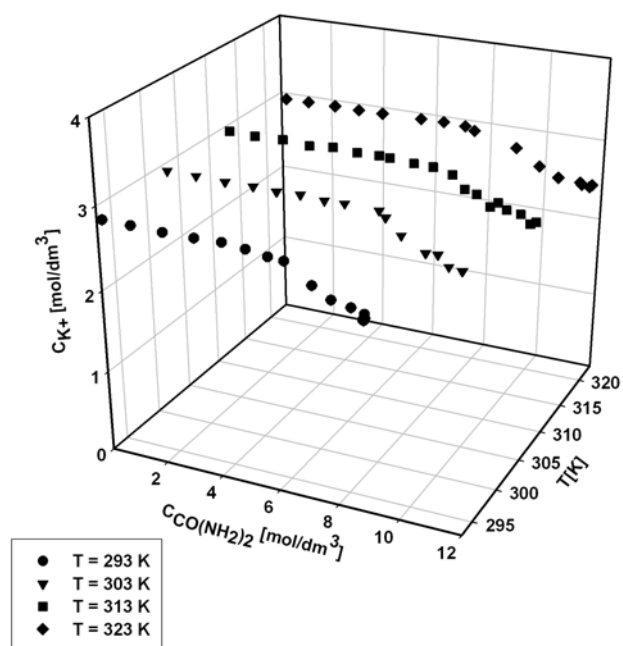


Figure 3. The course of the density changes dependence on the urea concentration in the temperature range of 293 – 323 K

**Analytical Methods:** The concentration of potassium ions in the equilibrium solutions was determined by gravimetric analysis via potassium tetraphenylborate ( $K[B(C_6H_5)_4]$ ) formed in the acidic solution (2 M HCl)<sup>11, 12</sup>. The average relative error of the measurement was estimated to be  $\pm 1.5\%$ .

The concentration of vanadium(V) was determined by using a spectrophotometric method<sup>13, 14</sup>. The formation of a coloured complex by the reaction of vanadium(V) with  $H_2O_2$  was employed. The analysis was performed using a double-beam UV-VIS spectrophotometer (Hitachi U-2000). The relative error was less than 2%.

The urea concentration in the equilibrium solutions was determined by the Kjeldahl method<sup>15, 16</sup>. The sample is heated to reach the boiling temperature in the presence of the concentrated sulfuric(VI) acid and catalyst agents ( $CuSO_4$ ). In order to increase the boiling temperature of the sample, potassium sulfate(VI) was added. The  $NH_4^+$  ions concentration was determined by a distillation method, using a fully automatic distillation apparatus Vapodest 30 (Gerhardt, Germany).

Ammonia was released from the solution using a strong base and was subsequently absorbed in the solution of sulfuric(VI) acid. Acid excess was then potentiometrically titrated with a known NaOH solution. A fully automatic titrator 716 DMS TITRINO was used with a combined glass electrode supplied by Methrom, Switzerland. The average relative error was estimated to be  $\pm 2\%$ .

The  $CO(NH_2)_2$  concentration was calculated from the difference between the total  $NH_4^+$  concentrations and the  $NH_4^+$  concentrations corresponding to  $NH_4VO_3$  which is equivalent to the total concentration of vanadium(V) in the solution.

**Identification of Solid Phases:** The identification of the solid phase in equilibrium with the mother solution was carried out by an X-ray method. Wet crystals were vacuum filtered with the use of a sintered glass crucible. The sample was dried at room temperature, grinded into powder, and then analysed by the X-ray method<sup>17</sup>. The analysis was employed on the X-ray diffraction analyzer PHILIPS X'Pert with  $CuK_\alpha$  radiation.

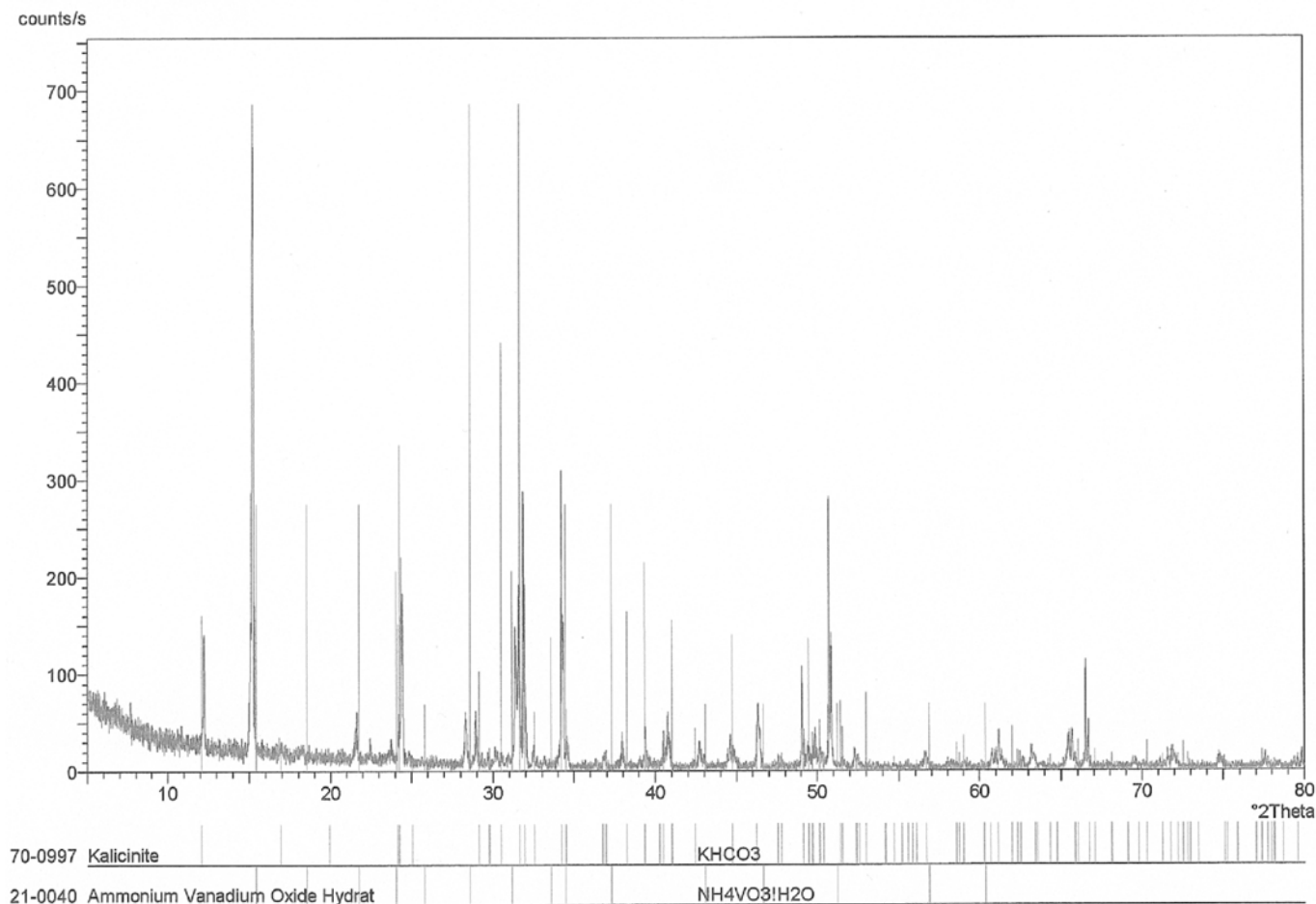
## RESULTS AND DISCUSSION

The results qualitative from the chemical analysis of the equilibrium solutions gave grounds for the construction of the solubility isotherm. For four different temperatures the concentration of both salts (Figures 1 and 2), the solution density (Figure 3) and the type of solid phase present, are reported.

Figure 1 shows the changes of vanadium(V) concentration as a function of the urea concentration and the temperature. The observed course of the curves plotted in Fig. 1 indicates that with the increasing concentration of  $CO(NH_2)_2$ , the vanadium(V) concentration is systematically decreased, which confirms the salting-out effect of urea on the ammonium metavanadate(V) solubility. The effect of decreasing the vanadium(V) concentration in the presence of urea is stronger at higher temperatures and at  $T = 323$  K the vanadium(V) concentration is decreased by 74%.

Figure 2 illustrates the changes of potassium ions concentration as a function of the urea concentration and the temperature. Fig. 2 indicates that there is small effect of the presence of urea on the potassium ions concentration. The potassium ions concentration is insignificantly decreased with the increasing  $CO(NH_2)_2$  concentration within the studied temperature range.

The experimental data were also used to show the relationship between the equilibrium solution density and the concentration of urea for the temperature range 293 – 323 K. Fig. 3 indicates that there is no effect of the urea presence on the solution density. The solution density is practically constant with the increasing  $CO(NH_2)_2$  concentration within the studied temperature range.



**Figure 4.** The X-ray diffraction pattern of the solid phase without urea at 323 K

The results obtained from X-ray analysis of the selected precipitates and the course of the plotted curves indicate that no new solid phase is formed in the investigated system. Over the temperature range studied, the equilibrium solid phase is composed of:  $\text{KHCO}_3$  and  $\text{NH}_4\text{VO}_3$  for points of urea unsaturated solution (Figure 4) and  $\text{KHCO}_3$ ,  $\text{NH}_4\text{VO}_3$  and  $\text{CO}(\text{NH}_2)_2$  for points with urea in solid phase (Figure 5).

The results of our research indicate that urea might be used successfully for minimizing the losses of toxic vanadium(V) compounds in the post-filtration liquor.

## CONCLUSION

1. Urea has a salting-out effect on the vanadium(V) concentration in its saturated solution. The effect is stronger at higher temperatures.

2. The presence of urea has a small effect on the potassium ions concentration.

3. The density of the equilibrium solution insignificantly decreases with the  $\text{CO}(\text{NH}_2)_2$  concentration.

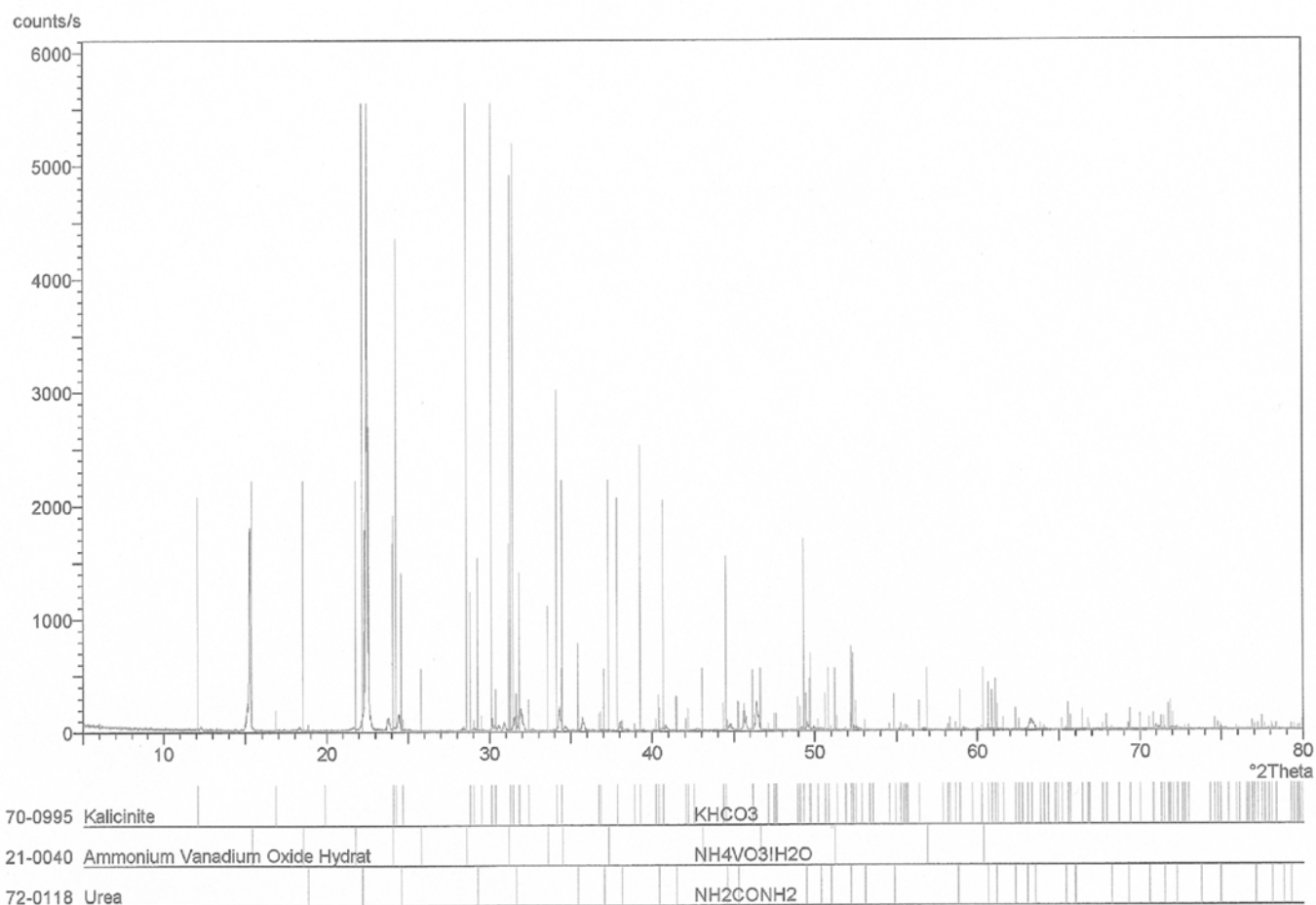
4. No new double salts or addition compounds are formed in the investigated system.

## AKNOWLEDGEMENT

This work is supported by KBN grant 3T09B12428

## LITERATURE CITED

- (1) Patent PL 186717, **2004**.
- (2) Trypuć M., Torski Z., Kielkowska U.: Experimental determination of the optimum conditions of  $\text{KVO}_3$  synthesis based on  $\text{KCl}$  and  $\text{V}_2\text{O}_5$  in the presence of steam, *Ind. Eng. Chem. Res.*, **2001**, 4, 1022.
- (3) Trypuć M., Białowicz K., Mazurek K.: Investigations on the synthesis of  $\text{KVO}_3$  and  $\text{Cl}_2$  from  $\text{KCl}$  and  $\text{V}_2\text{O}_5$  in presence of oxygen, *Chem. Eng. Science*, **2004**, 59/6, 1241.
- (4) Trypuć M., Kielkowska U., Białowicz K., Mazurek K.: Solubility of Ammonium Metavanadate in Potassium Bicarbonate Water Solution, *Pol. J. Chem. Tech.*, **2004**, 2, 53.
- (5) Kielkowska U., Trypuć M., Białowicz K., Mazurek K.: Wpływ stężenia wodorowęglanu potasu na rozpuszczalność metawanadanu(V) amonu w roztworach wodnych, *Przem. Chem.*, **2006**, 85/8 – 9, 831.
- (6) Сулајманкулов К.: Сојединения карбамида з неорганическимим солими. ИЛИМ, Москва, **1971**.
- (7) Samuskevich L. N., Petrowskaya L. I., Lunaeva N. K.: Temperature – dependent anionic composition of the  $\text{H}_3\text{PO}_4 - \text{CO}(\text{NH}_2)_2 - \text{H}_2\text{O}$  system: effect of inorganic salts, *Inorg. Mater.*, **1998**, 34, 293.
- (8) Loh W., Beezer A. E., Mitchell J. C.: Thermochemical investigations between urea and some sparingly soluble solutes in aqueous solution. *Tchermochimica acta*, **1995**, 255, **1995**.
- (9) Trypuć M., Białowicz K., Mazurek K., Kielkowska U.: Minimizing the losses of toxic vanadium compounds in the vanadium method by urea application, *Pol. J. Chem. Tech.*, **2004**, 2, 56.
- (10) Trypuć M., Kielkowska U., Stefanowicz D.: Solubility investigations in the  $\text{KHCO}_3 + \text{NH}_4\text{HCO}_3 + \text{H}_2\text{O}$  System, *J. Chem. Eng. Data*, **2001**, 46, 800.



**Figure 5.** The X-ray diffraction pattern of the solid phase with urea at 323 K

(11) Furman N. H.: Standard Method of Chemical Analysis, vol. I, Van Nostrand, Princeton, NJ, USA, **1962**.

(12) Struszyński M.: Analiza jakościowa i techniczna, PWT, Warszawa, Poland, **1982**.

(13) Sandell G.: Colorimetric metal analysis, Intersc. Publishers: New York, USA, **1959**.

(14) Williams W. J.: Handbook of Anion Determination, Butterworth, London, UK, **1979**.

(15) Minczewski J., Marczenko Z.: Chemia Analityczna, PWN, Warszawa, Poland, **1987**.

(16) Houben J., Weil Th.: Methoden der organischen Chemie, GT, Stuttgart, **1974**.

(17) Joint Committee on Powder Diffraction Standards, Powder Diffraction File, USA, **1976**.