*Polish Journal of Chemical Technology, 10, **4**, 25 — 27, 2008, 10.2478/v10026-008-0042-2*

The influence of urea on the K_2CO_3 and NH_4VO_3 solubility in the K_2CO_3 + NH_4VO_3 + H_2O system

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The influence of urea on the vanadium(V) and potassium ion concentrations in the K_2CO_3 + NH_4VO_3 + H_2O system was determined in the temperature range of 293 K to 313 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 vanadate(V), potassium carbonate, urea, water.

INTRODUCTION

Previous research projects have led to the development of an alternative production process of K_2CO_3 based on KVO_3[1 – 3]. Potassium vanadate(V) are generated from reactants: KCl and V_2O_5 in the presence of steam or oxygen. These processes can be described by the following chemical reactions:

$$2KCl(s) + V_2O_5(s) + 0.5O_2(g) \rightarrow 2KVO_3(s) + Cl_2(g) \quad (1)$$

$$2KCl(s) + V_2O_5(s) + H_2O(g) \rightarrow 2KVO_3(s) + 2HCl(g) \quad (2)$$

The formation of K_2CO_3 is based on carbonization of KVO_3 water + ammonia solutions (according to reaction 3 and 4)[4, 5]. As a result, a sparingly soluble precipitate of NH_4VO_3 is obtained, whereas a mixture of $KHCO_3$ and K_2CO_3 remains in solution. The carbonization degree [R] (R – is defined as the ratio of the CO_2 concentration in the form of HCO_3^- ions to solution alkalinity) of the solution influences the ratio of the concentration of the coexisting salts.

$$KVO_3 + NH_3 + CO_2 + H_2O \leftrightarrow NH_4VO_3 + KHCO_3 \quad (3)$$

$$2KVO_3 + 2NH_3 + CO_2 + H_2O \leftrightarrow 2NH_4VO_3 + K_2CO_3 \quad (4)$$

The research conducted by Pieniążek on the system KCl – $MgSO_4$ – K_2SO_4 – $MgCl_2$ – H_2O in the presence of urea revealed that the reaction yield of the K_2SO_4 synthesis is significantly increased, especially for higher $CO(NH_2)_2$ concentrations[6, 7]. This yield increase is mainly caused by the generation of the binary compound $MgCl_2 \cdot 4CO(NH_2)_2$ in the equilibrium solution which has a higher solubility than $MgCl_2$, when urea is not present.

Similar results have been reported by Trypuć for the KCl – NH_3 – CO_2 – H_2O system in the presence of urea[8]. It was found that the carbonization yield in relation to potassium ion species at the triple point P_1 (P_1 – triple point, where the solution is in equilibrium with three solids) increased significantly in the presence of urea, as compared to the detected yield without urea present.

This paper is a continuation of the studies to determine the solubility of vanadium, potassium and ammonium salts in the presence of urea[9 – 11]. Knowledge of the solubility of NH_4VO_3 and K_2CO_3 in the presence of $CO(NH_2)_2$ is needed for the separation of residual NH_4VO_3 out of the post – filtration liquor and subsequent evaporation to obtain pure K_2CO_3.

So far, no literature data on the solubility of NH_4VO_3 + K_2CO_3 + H_2O system in the presence of urea has been found.

EXPERIMENTAL

Materials

Analytical pure chemicals: NH_4VO_3 (purity of 99%, Aldrich), K_2CO_3 (purity of 99.98%, POCh Gliwice S.A., Poland) and $CO(NH_2)_2$ (purity of 99.5%, POCh Gliwice S.A., Poland) were used for all the experiments, without further purification.

Experimental Procedure

The solubility measurements for the ammonium vanadate(V) + potassium carbonate + water system in the presence of urea were carried out at 293 to 313 K, respectively, using the isothermal solution saturation method.

Each component of the studied system was placed in the thermostated Erlenmeyer flasks of 100 cm^3 capacity. Next, the samples were transferred to a thermostated bath and stirred magnetically for 120 hours. This procedure guaranteed the equilibrium between the solution and the solid phase at the respective temperature.

The temperature was maintained constant applying the BIOBLOCK-SCIENTIFIC thermorelay with an accuracy of ± 0.02 K. Additionally, the temperature was measured using a mercury thermometer with accuracy of ± 0.05 K.

After the desired time interval, stirring was discontinued and the solutions were left for the solid phase to settle. The clear solution was sampled into a calibrated Ostwald pycnometer. Sampling was performed under slight overpressure conditions produced by a mini sample – injector pump. This technique enabled precise sampling without the danger of crystallization.

The entire content of the pycnometer was used for the determination of the density of the equilibrium solution. The density measurements were performed with the accuracy of $\pm$ 0.002 $g \cdot cm^{-3}$.

Next, the pycnometer content was transferred quantitatively to the flasks and diluted with an adequate amount of distilled water. Then a chemical analysis was carried out to determine the concentration of the salts.

After the density determination, the slight under-pressure conditions were applied during the transfer of the pycnometer contents to the flasks. Other methods of transfer fail because of the solutes crystallization.

Analytical Methods

The concentration of potassium ions in equilibrium solutions was determined by the gravimetric analysis via potassium tetraphenyloborate ($K[B(C_6H_5)_4]$) formed in acidic solution (2 M HCl)[12, 13]. The average relative error of the measurement was estimated to be ± 2%.

The concentration of vanadium(V) was determined by using a spectrophotometric method[14, 15]. 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 equilibrium solutions was determined by the Kjeldahl method[16]. The sample is heated to reach the boiling temperature in the presence of 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 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 a solution of sulfuric(VI) acid. Acid excess was then potentiometrically titrated with a known NaOH solution. A fully automatic titrator Titroline alpha was used with a combined glass electrode supplied by Schott Geräte, Germany. The average relative error was estimated to be ± 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.

RESULTS AND DISCUSSION

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

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 vanadate(V) solubility in this system. The effect of decreasing the vanadium(V) concentration in the presence of urea is stronger at higher temperatures and at T = 313 K the vanadium(V) concentration is decreased by 60%.

Figure 2 implies clearly that there is no effect of urea presence on the K^+ solubility. The K^+ ions concentration is practically constant with increasing concentration of urea over the studied temperature range in the studied system.

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 – 313 K. Fig. 3 indicates that there is a small effect of the urea presence on the solution density. The solution density is slightly decreased with the increasing $CO(NH_2)_2$ concentration within the studied temperature range.

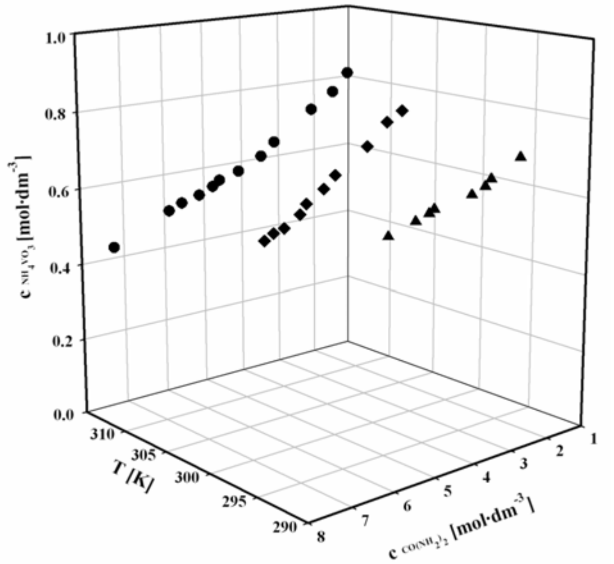

Figure 1. The vanadium(V) concentration dependence on the urea concentration at three different temperatures: 293 K, 303 K, 313 K

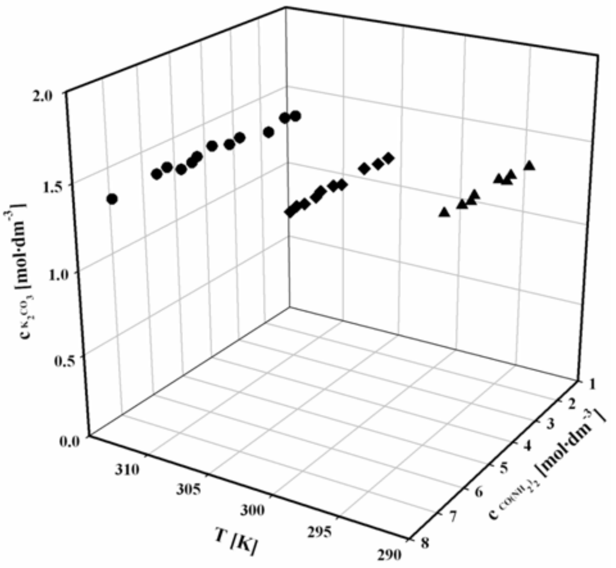

Figure 2. The potassium carbonate concentration dependence on the urea concentration and temperature

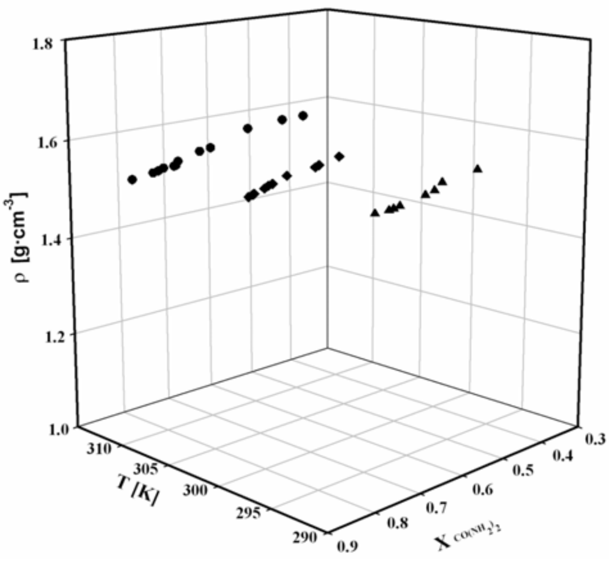

Figure 3. The course of the density changes dependence on the urea concentration in the temperature range of 293 – 313 K

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

CONCLUSION

1. Urea has a salting-out effect on the vanadium(V) concentration in the studied system. The effect is stronger at higher temperatures.
2. The presence of urea has no effect on the potassium ions concentration.
3. The density of the equilibrium solution insignificantly decreases with the increasing $CO(NH_2)_2$ concentration.
4. No new double salts or addition compounds are formed in the investigated system.

AKNOWLEDGEMENT

This work is supported by KBN grant 3T09B12428

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