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SOLUBILITY IN THE $KVO_3 + NH_3 + CO_2 + H_2O$ SYSTEM FROM 293K TO 303K

ROZPUSZCZALNOŚĆ W UKŁADZIE $KVO_3 + NH_3 + CO_2 + H_2O$ W ZAKRESIE TEMPERATUR 293–303K

A b s t r a c t

Solubility in the $KVO_3 + NH_3 + CO_2 + H_2O$ system and the saturated solution densities were measured employing the isothermal solution saturation method. Investigations in the given range of the NH_3 concentration varying from 0.1 to 0.6 mol·dm^{-3}, as a function of time and temperature, have been carried out. The data presented herein is essential for the assessment of optimum operating conditions for the production process of potassium carbonate introducing the modified Solvay's method.

Keywords: potassium metavanadate(V), ammonia, solubility, equilibrium

S t r e s z c z e n i e

Metodą izotermicznego nasycania roztworów zbadano rozpuszczalność i oznaczono gęstość roztworów równowagowych w układzie $KVO_3 + NH_3 + CO_2 + H_2O$. Badania prowadzono w zakresie stężeń NH_3 od 0,1 to 0,6 mol·dm^{-3}, w zależnośvi od czasu i temperatury. Uzyskane dane są niezbędne przy opracowaniu optymalnych parametrów otrzymywania węglanu potasu zmodyfikowaną metodą Solvaya.

Słowa kluczowe: metawanadan potasu, amoniak, rozpuszczalność, równowaga

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1. Introduction

Further investigations revealed a potential possibility of K_2CO_3 production based on the carbonization of KVO_3 + ammonia solutions [1].

KVO_3 is generated from KCl and V_2O_5 in the presence of steam or oxygen according to the reactions given below [2–4]

$$2\ KCl + V_2O_5 + H_2O_{(steam)} \rightarrow 2\ KVO_3 + 2\ HCl \quad (1)$$

$$4\ KCl + 2\ V_2O_5 + O_2 \rightarrow 4\ KVO_3 + 2\ Cl2 \quad (2)$$

K_2CO_3 production process can be described by a general equation

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

The process of carbonization of water + ammonia solution of KVO_3, consisting of polythermic-polybaric chemisorption of carbon dioxide and crystallization of ammonium metavanadate is a very important step of the vanadate method of K_2CO_3 production.

Knowledge of the solubility in the systems: $KVO_3 + H_2O$ [5, 6], $KVO_3 + NH_3 + H_2O$ [7] and $KVO_3 + NH_3 + CO_2 + H_2O$ is essential for the assessment of optimum operating conditions for the carbonization step in the production process of potassium carbonate.

Since the literature inspection has not revealed any solubility data describing the KVO_3 solubility in aqueous ammonia solutions partially carbonating the equilibrium studies have been undertaken to present a comprehensive and reliable report.

2. Experimental Part

Analytical purity grade chemicals were used for all of the experiments: KVO_3 (purity of 98%, Aldrich Chemical Company, Inc.) and NH_3 (Nitrogen Works Tarnów-Mościce SA, Poland).

Investigations on the solubility of potassium metavanadate(V) in water + ammonia + carbon dioxide solutions in the given range of the NH_3 concentration varying from 0.1 to 0.6 $mol \cdot dm^{-3}$, as a function of temperature and time, have been carried out. The experiments were performed in the temperature range from 293 to 303K.

The required amounts of salt and water + ammonia solutions were thermostated at a selected temperature in the time range from 24 to 96 h, with constant stirring.

At both the temperatures of 293K and 303K, a CO_2 partial pressure of about 1 atm was required. All of the laboratory tests were carried out in the originally constructed pressure apparatus, which both guaranteed operational safety and enabled to reach the state of equilibrium [8].

After equilibration the clear solution was sampled to chemical analysis to determine the solution density. The accuracy of that determination was ± 0.002 $g \cdot cm^{-3}$.

The concentration of vanadium(V) in the equilibrated solutions was determined by a spectrophotometric analysis using the peroxide method [5, 9, 10]. The analysis was

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performed with the double-beam UV-VIS HITACHI U-2000 spectrophotometer. The error of the vanadium determination is approximately of 2%.

The potassium ion concentration was determined by weight with sodium tetraphenylborate ($Na[B(C_6H_5)_4]$) as a precipitating agent [9]. The precision of the measurements was estimated within 1%.

Concentration of the water + ammonia solutions was determined with the automatic distillation apparatus VAPODEST 30 [11, 12]. The precision of the measurements was estimated within 1%.

The CO_2 concentration of the given solutions was determined using the originally built apparatus described earlier [13]. Quantitatively generated CO_2 gas was absorbed by a NaOH test solution, then $BaCl_2$ solution was added to precipitate $BaCO_3$ out. The excess of NaOH solution was titrated with an acid in the presence of mixed acid-base indicators (thymol blue + cresol red). Finally, methyl orange was introduced and CO_2 determined by titration of $BaCO_3$ solids with a diluted HCl solution. The experimental procedures have been previously reported in detail [13].

The identification of the solid phases equilibrated with the mother solution was carried out by an X-ray method [14].

3. Results and Discussion

We have found that substrates in the investigated system react and the insoluble ammonium metavanadate(V) is produced. The similar effect was also observed in the research on the $NaVO_3$ [11] and KVO_3 [7] solubility in the aqueous solutions of ammonia without carbon dioxide.

Table 1

KVO_3 solubility in the $KVO_3 + NH_3 + CO_2 + H_2O$ at 293K

Time [h]	$c(K^+)$ [mol·dm^{-3}]	$c(VO_3^-)$ [mol·dm^{-3}]	$c(NH_4^+)$ [mol·dm^{-3}]	$c(CO_2)$ [mol·dm^{-3}]
$c(NH_3$ init) = 0.1 mol·dm^{-3}				
24	0.6938	0.5947	0.0334	0.1615
48	0.7398	0.6304	0.0378	0.2310
72	0.7772	0.6567	0.0670	0.1870
96	0.8283	0.6922	0.0437	0.2003
$c(NH_3$ init) = 0.3 mol·dm^{-3}				
24	0.7189	0.4774	0.1440	0.1949
48	0.7061	0.4268	0.1224	0.2645
72	0.7501	0.4447	0.1282	0.2974
96	0.7833	0.4710	0.1279	0.1926
$c(NH_3$ init) = 0.6 mol·dm^{-3}				
24	0.7649	0.3353	0.1737	0.2435
48	0.8043	0.3577	0.1679	0.2356
72	0.8923	0.3559	0.1798	0.2769
96	0.8723	0.3357	0.1574	0.2850

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As long as KVO_3 is the only salt remaining in an equilibrium with the solution, $[K^+] = [VO_3^-]$. When the first ammonium metavanadate(V) crystals are formed $[K^+] > [VO_3^-]$.

Analyses for K^+, VO_3^- and NH_3 are necessary to characterize the system. The results of the chemical analyses of the solutions are presented in Tables 1 and 2.

Table 2

KVO_3 solubility in the $KVO_3 + NH_3 + CO_2 + H_2O$ at 303K

Time [h]	$c(K^+)$ [mol·dm^{-3}]	$c(VO_3^-)$ [mol·dm^{-3}]	$c(NH_4^+)$ [mol·dm^{-3}]	$c(CO_2)$ [mol·dm^{-3}]
$c(NH_3$ init) = 0.1 mol·dm^{-3}				
24	0.8668	0.8228	0.1096	0.1762
48	0.8641	0.8291	0.1024	0.1269
72	0.9404	0.8646	0.0863	0.1206
96	0.9328	0.8453	0.0863	0.1276
$c(NH_3$ init) = 0.3 mol·dm^{-3}				
24	0.8839	0.6814	0.1634	0.2589
48	0.9251	0.7227	0.1796	0.3073
72	0.9370	0.7505	0.1446	0.2289
96	0.9463	0.7127	0.1563	0.1844
$c(NH_3$ init) = 0.6 mol·dm^{-3}				
24	0.9863	0.6331	0.1913	0.2032
48	1.0358	0.6608	0.1913	0.2415
72	1.0474	0.6705	0.1971	0.2739
96	1.0330	0.6532	0.1913	0.2342

We found that the concentration of potassium ions in the equilibrated solutions rises with the increasing NH_3 concentration and time at the investigated temperature range.

The results also reveal that the KVO_3 solubility increases with the temperature elevation at the whole range of NH_3 concentrations in the solution.

Based on the experimental data, the ratio of KVO_3 conversion into NH_4VO_3 might be calculated according to the following ion concentration proportion

$$[K^+] - [VO_3^-] / [K^+] \tag{4}$$

The dependence of the conversion ratio of potassium metavanadate(V) into ammonium metavanadate(V) calculated from equation (4), on the initial NH_3 concentration, time and temperature is presented in Table 3. Analysis of these data shows that the conversion ratio of KVO_3 into NH_4VO_3 rises with the increase of NH_3 concentration and the time of thermostating. We found that the conversion ratio decreases with the increase of temperature.

The course of the density changes dependence on the initial NH_3 concentration and the time at both temperatures is presented in Figs 1 and 2.

The X-ray analysis of the solid phase revealed that for all the investigated samples, the precipitate remaining in equilibrium with the solution is a mixture of NH_4VO_3 and KVO_3.

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Table 3

KVO_3 conversion ratio into NH_4VO_3

c(NH_3 init) [mol·dm^{-3}]	Time [h]	Conversion ratio
T = 293K		
0.1	24	0.1428
	48	0.1479
	72	0.1551
	96	0.1643
0.3	24	0.3359
	48	0.3956
	72	0.4072
	96	0.3986
0.6	24	0.5617
	48	0.5552
	72	0.6012
	96	0.6153
T = 303K		
0.1	24	0.0507
	48	0.0405
	72	0.0806
	96	0.0938
0.3	24	0.2291
	48	0.2188
	72	0.1990
	96	0.2469
0.6	24	0.3581
	48	0.3621
	72	0.3598
	96	0.3677

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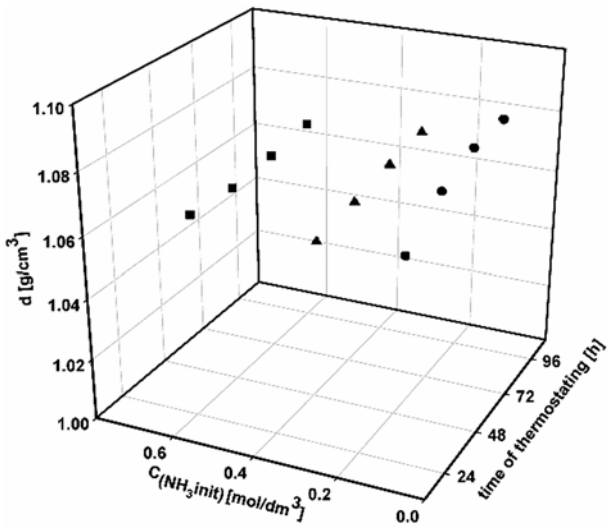

Fig. 1. Course of the density changes dependence on the initial NH_3 concentration and time at 293K: (•) – 0.1 mol/dm^3, (▼) – 0.3 mol/dm^3, (■) – 0.6 mol/dm^3

Rys. 1. Zmiany gęstości roztworów w zależności od stężenia początkowego NH_3 i czasu w temperaturze 293K: (•) – 0,1 mol/dm^3, (▼) – 0,3 mol/dm^3, (■) – 0,6 mol/dm^3

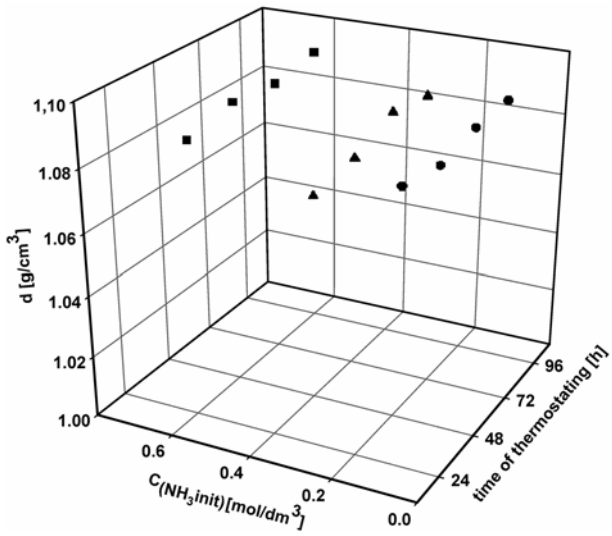

Fig. 2. Course of the density changes dependence on the initial NH_3 concentration and time at 303K: (•) – 0.1 mol/dm^3, (▼) – 0.3 mol/dm^3, (■) – 0.6 mol/dm^3

Rys. 2. Zmiany gęstości roztworów w zależności od stężenia początkowego NH_3 i czasu w temperaturze 303K: (•) – 0,1 mol/dm^3, (▼) – 0,3 mol/dm^3, (■) – 0,6 mol/dm^3

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