Articles

Solubility Investigations in the $Na_2SO_4 + V_2O_5 + H_2O$ System from 293 K to 323 K

Mieczysław Trypuć, Małgorzata Chałat, and Krzysztof Mazurek*

Faculty of Chemistry, Nicolaus Copernicus University, 7 Gagarin Street, 87-100 Toruñ, Poland

Mutual solubility of Na_2SO_4 and V_2O_5 in water at the temperature range (293 to 323) K was investigated by the method of isothermal saturation. The vanadate ion concentration was determined by a spectrophotometric analysis using 4-(2-pyridylazo)resorcinol, concentration of sulfate ions by a gravimetric method as $BaSO_4$, and the sodium ion concentration was determined by an atomic absorption spectrometry method. On the basis of the results, the section of the solubility polytherm for the $Na_2SO_4 + V_2O_5 + H_2O$ system was plotted. These data can be used to assess the possibility to utilize vanadium(V) oxide from the vanadate catalyst used in the process of SO_2 to SO_3 oxidation for the synthesis of Na_2CO_3 or K_2CO_3.

Introduction

The research on the possibility of the use of vanadium compounds in the production of soda and potash has continued for several years.[1] Aarts first introduced the idea in 1967.[2] The basis for that idea was the necessity of the intermediate reagent reacting with NaCl to generate the product that would not contain chloride ions and could be easily transformed into Na_2CO_3. Such an intermediate reagent should be fully recycled in the process. The research showed that V_2O_5 would be most suitable for that purpose. Vanadium(V) oxide reacts with sodium chloride in a presence of oxygen or steam, producing sodium vanadate(V) and chlorine or hydrogen chloride, respectively. The produced $NaVO_3$ may be used for the production of soda in a process analogous to the Solvay method. Preliminary research showed that a similar method might be used for the production of potassium carbonate from KCl and V_2O_5.[3]

Although Aarts presented the set of chemical reactions leading to the formation of soda and chlorine or hydrogen chloride from NaCl using the vanadate method, he never confirmed experimentally the possibility of its practical use. The research of our group allowed determination of the optimal parameters for syntheses of $NaVO_3$ from NaCl and V_2O_5 or KVO_3 from KCl and V_2O_5 with the use of oxygen or steam[4−11] as well as the optimal parameters for carbonization of $NaVO_3$ and KVO_3 solutions.[12−18] We have also investigated the conditions of ammonization of $NaVO_3$[19] and KVO_3 as well as the kinetics of NH_4VO_3 precipitation from the post-carbonization solution.

The fundamental conditions for the industrial use of the proposed method would be the low price of the product, its high quality, and its low environmental impact. Certainly the significant economic disadvantage of the proposed vanadate method in Poland would be the lack of natural deposits of vanadium compounds and their high market prices.

One of the investigated options was the utilization of used vanadate catalysts from the sulfuric acid production by the contact process directly for the synthesis of sodium or potassium metavanadates from NaCl or KCl. The used catalyst, besides vanadium(V) oxide (ca. 7 % of the contact mass), contains also different sodium, potassium, and sulfur compounds.[20,21]

Economical control of the $NaVO_3$ and KVO_3 synthesis from the used vanadate catalyst would require the complete isolation of the product and recovery of the unreacted vanadium(V) oxide from the post-reaction mixture. Therefore, it is important to investigate the influence of the presence of different vanadate catalyst components on the solubility of vanadium(V) compounds in aqueous solutions. The results reported here present the data on the components solubility in the $Na_2SO_4 + V_2O_5 + H_2O$ system at the temperature range (293 to 323) K.

Experimental Section

Chemicals. The research was performed with the use of Na_2SO_4 (pure for analysis, POCh Gliwice, Poland) and V_2O_5 (98 %, Aldrich Chemical Co., Inc.).

Experimental Procedure. The mutual solubility in the system sodium sulfate + vanadium(V) oxide + water was investigated at 293 K, 303 K, 313 K, and 323 K by the isothermal saturation method.

Each mixture containing the required amount of reagents and distilled water was thermostated in the Erlenmeyer flasks of 100 cm^3 capacity. During that process, the solutions were stirred with a magnetic stirrer. The temperature was kept constant with the use of thermorelay Polystat CC 1 (Germany) with an uncertainty of ± 0.02 K. The equilibration time was experimentally determined to be not shorter than 1 week. This procedure guaranteed the equilibrium between solution and the solid phase at the respective temperature.

The stirring was stopped after that time to allow the precipitate to sediment. Then the equilibrated solution was transferred to the Ostwald pycnometer and calibrated at the selected temperature. Sampling was performed at slight overpressure conditions produced by a mini-sample−injector pump. This technique enabled precise sampling without danger of crystallization.

---

* Corresponding author. E-mail: mazur@chem.uni.torun.pl. Phone: +(48)566114569. Fax: +(48)566542477.

10.1021/je050233b CCC: $33.50

Table 1. Experimental Results for the Mutual Solubility of Na_2SO_4 and V_2O_5 in Water

	c/mol·dm^{-3}		
ρ/g·dm^{-3}	V_2O_5	Na_2SO_4	solid phase
		$T = 293$ K	
1.142	0.00	1.31	$Na_2SO_4 \cdot 10\ H_2O$
1.139	$1.15 \cdot 10^{-4}$	1.31	$Na_2SO_4 \cdot 10\ H_2O$
1.143	$2.38 \cdot 10^{-4}$	1.32	$Na_2SO_4 \cdot 10\ H_2O$
1.139	$3.83 \cdot 10^{-4}$	1.33	$Na_2SO_4 \cdot 10\ H_2O$
1.140	$4.50 \cdot 10^{-4}$	1.34	$Na_2SO_4 \cdot 10\ H_2O$
1.145	$6.05 \cdot 10^{-4}$	1.33	$Na_2SO_4 \cdot 10\ H_2O$, V_2O_5
1.132	$6.11 \cdot 10^{-4}$	1.12	V_2O_5
1.111	$6.33 \cdot 10^{-4}$	0.94	V_2O_5
1.076	$7.41 \cdot 10^{-4}$	0.68	V_2O_5
1.057	$8.56 \cdot 10^{-4}$	0.48	V_2O_5
1.032	$9.95 \cdot 10^{-4}$	0.29	V_2O_5
1.024	$1.20 \cdot 10^{-3}$	0.20	V_2O_5
1.012	$1.49 \cdot 10^{-3}$	0.12	V_2O_5
1.002	$1.87 \cdot 10^{-3}$	0.01	V_2O_5
0.997	$2.05 \cdot 10^{-3}$	0.00	V_2O_5
		$T = 303$ K	
1.257	0.00	2.48	$Na_2SO_4 \cdot 10H_2O$
1.261	$1.09 \cdot 10^{-4}$	2.48	$Na_2SO_4 \cdot 10H_2O$
1.265	$2.00 \cdot 10^{-4}$	2.49	$Na_2SO_4 \cdot 10H_2O$
1.261	$2.92 \cdot 10^{-4}$	2.49	$Na_2SO_4 \cdot 10H_2O$
1.269	$4.00 \cdot 10^{-4}$	2.49	$Na_2SO_4 \cdot 10H_2O$
1.267	$4.62 \cdot 10^{-4}$	2.50	$Na_2SO_4 \cdot 10H_2O$, V_2O_5
1.163	$4.82 \cdot 10^{-4}$	1.76	V_2O_5
1.120	$5.10 \cdot 10^{-4}$	1.11	V_2O_5
1.082	$5.77 \cdot 10^{-4}$	0.86	V_2O_5
1.032	$7.81 \cdot 10^{-4}$	0.32	V_2O_5
1.010	$1.10 \cdot 10^{-3}$	0.15	V_2O_5
1.002	$1.42 \cdot 10^{-3}$	0.03	V_2O_5
1.000	$1.80 \cdot 10^{-3}$	0.01	V_2O_5
0.998	$2.16 \cdot 10^{-3}$	0.00	V_2O_5
		$T = 313$ K	
1.317	0.00	3.05	Na_2SO_4
1.319	$9.57 \cdot 10^{-5}$	3.07	Na_2SO_4
1.318	$1.21 \cdot 10^{-4}$	3.08	Na_2SO_4
1.319	$2.22 \cdot 10^{-4}$	3.10	Na_2SO_4
1.320	$2.74 \cdot 10^{-4}$	3.10	Na_2SO_4
1.320	$3.27 \cdot 10^{-4}$	3.11	Na_2SO_4, V_2O_5
1.243	$3.46 \cdot 10^{-4}$	2.32	V_2O_5
1.110	$4.09 \cdot 10^{-4}$	1.52	V_2O_5
1.081	$4.82 \cdot 10^{-4}$	0.78	V_2O_5
1.030	$7.81 \cdot 10^{-4}$	0.21	V_2O_5
1.009	$1.22 \cdot 10^{-3}$	0.09	V_2O_5
1.001	$1.56 \cdot 10^{-3}$	0.04	V_2O_5
1.000	$1.89 \cdot 10^{-3}$	0.01	V_2O_5
0.999	$2.19 \cdot 10^{-3}$	0.00	V_2O_5
		$T = 323$ K	
1.305	0.00	2.95	Na_2SO_4
1.304	$5.40 \cdot 10^{-5}$	2.96	Na_2SO_4
1.303	$1.34 \cdot 10^{-4}$	2.99	Na_2SO_4
1.306	$1.51 \cdot 10^{-4}$	3.00	Na_2SO_4
1.304	$1.89 \cdot 10^{-4}$	3.01	Na_2SO_4
1.301	$2.20 \cdot 10^{-4}$	3.03	Na_2SO_4, V_2O_5
1.275	$2.24 \cdot 10^{-4}$	2.66	V_2O_5
1.224	$2.58 \cdot 10^{-4}$	2.18	V_2O_5
1.150	$2.79 \cdot 10^{-4}$	1.57	V_2O_5
1.090	$3.33 \cdot 10^{-4}$	0.78	V_2O_5
1.043	$5.77 \cdot 10^{-4}$	0.23	V_2O_5
1.012	$1.14 \cdot 10^{-3}$	0.03	V_2O_5
1.009	$1.52 \cdot 10^{-3}$	0.02	V_2O_5
1.003	$1.90 \cdot 10^{-3}$	0.01	V_2O_5
0.999	$2.22 \cdot 10^{-3}$	0.00	V_2O_5

The content of a pycnometer was used for a density determination with an uncertainty of ± 0.002 g·cm^{-3}. Next, the pycnometer contents was transferred quantitatively to the flasks, diluted with the adequate amount of distilled water, and analyzed to determine the concentration of different components. On completion of the whole process, slight under-pressure conditions were applied while the pycnometer's content was transferred to a graduated flask.

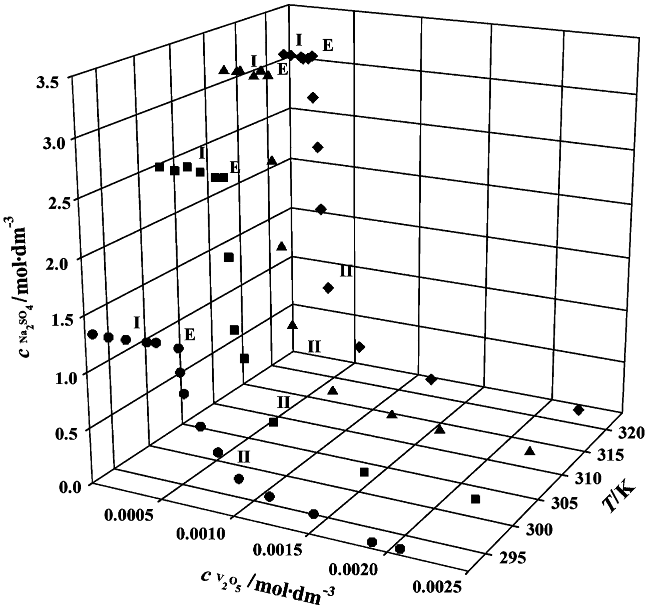

Figure 1. Solubility of Na_2SO_4 and V_2O_5 in the system $Na_2SO_4 + V_2O_5 + H_2O$.

Analytical Methods. The concentration of sulfate ions (≥ 0.20 mol·dm^{-3}) was determined by a gravimetric method. The sulfate ions were precipitated as barium sulfate(VI) with the use of barium chloride in the dilute solution of hydrochloric acid, filtered, washed, and roasted. The obtained precipitate $BaSO_4$ was then weighted.[22] All measurements were performed in triplicate, and the uncertainty of the analysis was estimated to be ± 2 %.

For the low concentrations of sodium sulfate(VI) (≤ 0.20 mol·dm^{-3}), the concentration of sodium ions was determined by the atomic absorption method[23] with the Varian spectrometer AAS Spectra-20 ABQ.

Before each series of analyses, the standardization curve of the absorption−concentration dependence was prepared for the Na^+ concentration range ($5 \cdot 10^{-5}$ to $1 \cdot 10^{-4}$) mol·dm^{-3}. The standard solutions for calibration were prepared by diluting the 0.01 mol·dm^{-3} solution of Na_2SO_4. The wavelength used was $\lambda = 589$ nm. The spectrometer aperture, gas flow, and electric current intensity for the lamp with the hollow cathode were set according to the values suggested in the manual. The apparatus was equipped with the flame burner supplied with the compressed air-acetylene mixture.

After suitable dilution, the concentration of sodium ions in each solution was determined based on the equation of the calibration curve. The measurements were carried out three times, and the uncertainty of the analysis was estimated to be ± 3 %.

The vanadium(V) concentration was determined by spectrophotometric analysis using the double-beam UV/VIS Hitachi U-2000 spectrophotometer. The analysis was based on the ability of vanadium(V) to form the colored complex with 4-(2-pyridylazo)resorcinol (PAR)[24−26] that is one of the most sensitive reagents for vanadium analyses. Beer's law is satisfied in the broad range of vanadium concentration ($2 \cdot 10^{-5}$ to $1.8 \cdot 10^{-2}$) mol·dm^{-3}. The optimal pH for that complex stability is pH = (5 to 6). The maximum absorption for that complex is at $\lambda = 543$ nm. The sodium salt of PAR was used because its higher solubility in water. All measurements were performed in triplicate, and the uncertainty of the analysis was estimated to be ± 2 %.

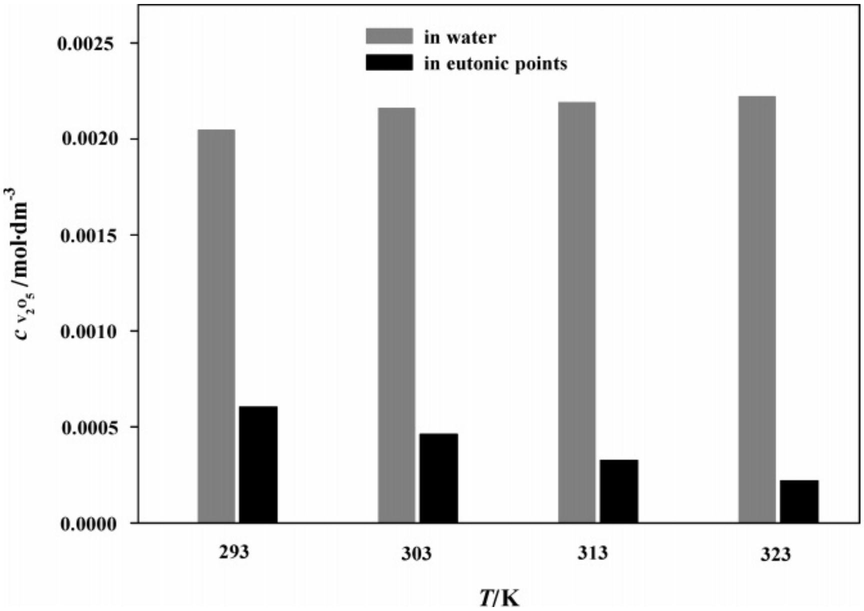

Figure 2. Comparison of the V_2O_5 solubility in the aqueous solutions and in the eutonic points.

The X-ray powder diffractometer Philips X'Pert PRO was used for the solid-phase identification by the $I = f(\theta)$ diffractogram analyses. The diffractograms were analyzed by comparison of the series of interplanar distances *d* and relative intensities *I* with those published in the database.[27,28]

Results and Discussion

The results of the quantitative analyses of the equilibrated solutions are presented in Table 1. The presented data allowed us to plot the section of the solubility polytherm in the $Na_2SO_4 + V_2O_5 + H_2O$ system (Figure 1).

Each isotherm consists of two branches. Branch I of each solubility isotherm corresponds to the saturated sodium sulfate(VI) solution and visualizes the changes of the Na_2SO_4 concentration with the increasing concentration of vanadium(V) oxide in the equilibrated solution. They begin at the points corresponding to the saturated solutions of pure Na_2SO_4 at a specific temperature and end at the eutonic points.

Branch II of the isotherms correspond to the saturated solutions of vanadium(V) oxide and reflect changes of the V_2O_5 concentration with the increasing concentration of sodium sulfate(VI) in the equilibrium solutions. The starting points correspond to the saturated solutions of V_2O_5 at the specific temperature, while their end points correspond to the eutonic points.

The eutonic points correspond to the solutions saturated with both Na_2SO_4 and V_2O_5. The solubility isotherms indicate that the increase of the vanadium(V) oxide concentration toward the eutonic points for the solutions saturated with Na_2SO_4 does not influence the sodium sulfate(VI) solubility in the equilibrium solutions. Differences between the Na_2SO_4 solubility in the aqueous solutions and in the eutonic points are (0.021, 0.013, 0.057, and 0.08) mol·dm^{-3} at (293, 303, 313, and 323) K, respectively.

The course of the isotherm branches II indicate that the addition of sodium sulfate(VI) to the saturated vanadium(V) oxide solution decreases the V_2O_5 solubility. The rapid decrease of the vanadium(V) oxide concentration is observed with the concentration of Na_2SO_4 increasing toward the eutonic points at the investigated temperature range. The differences in the V_2O_5 solubility between the aqueous solutions and the eutonic points are ($1.44 \cdot 10^{-3}$, $1.70 \cdot 10^{-3}$, $1.94 \cdot 10^{-3}$, and $2.00 \cdot 10^{-3}$) mol·dm^{-3} for (293, 303, 313, and 323) K, respectively (Figure 2). The decrease of the V_2O_5 solubility caused by the presence of sodium sulfate(VI) in the equilibrium solutions raises with the increasing temperatures.

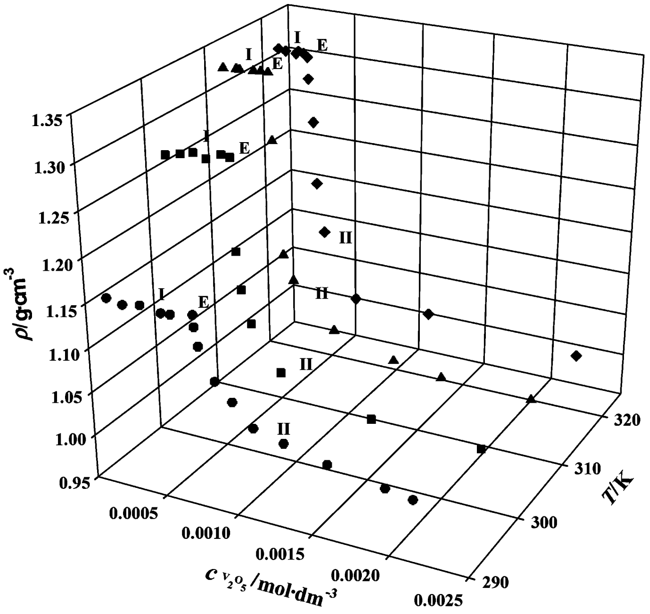

Figure 3. Solution density changes vs the V_2O_5 concentration at four different temperatures.

Analysis indicates that the Na_2SO_4 solubility in water increases with the raising temperature at the temperature range (293 to 313) K and slightly decreases at $T = 323$ K, which is in good agreement with the literature.[29] The concentration of V_2O_5 at 323 K was found higher by 8.5 % than that at 293 K.

Comparison of the solution densities (Figure 3) indicate that at each investigated temperature the density of the equilibrium solutions saturated with Na_2SO_4 does not change with the increasing concentrations of vanadium(V) oxide. The density of solutions saturated with V_2O_5 increases toward the eutonic points with the increasing concentration of Na_2SO_4.

The presence of a single eutonic point for each isotherm and the results of the X-ray analyses of the solid phases equilibrated with the solutions proved that no new phase is formed in the investigated system. The X-ray analyses proved that the solid phases remaining in the equilibrium with the solution consist of the following:

(i) At 293 and 303 K: for branch I, $Na_2SO_4 \cdot 10H_2O$; for branch II, V_2O_5; for eutonic points, $Na_2SO_4 \cdot 10H_2O + V_2O_5$.

(ii) At 313 and 323 K: for branch I, Na_2SO_4; for branch II, V_2O_5; for eutonic points, $Na_2SO_4 + V_2O_5$.

Literature Cited

(1) Trypuć, M. Vanadium method production of K_2CO_3. *Przem. Chem.* **2003**, *8−9*, 870−871.
(2) Aarts, W. H. Process for the production of sodium carbonate and hydrochloric acid and/or chlorine. U.S. Patent 3313593, 1967.
(3) Trypuć, M.; Stefanowicz, D.; Kiełkowska, U.; Łjak, G.; Torski, Z. Potassium carbonate production methods. RP Patent RP/4242/98, 1998.
(4) Trypuć, M.; Białowicz, K.; Mazurek, K. Investigations on the synthesis of $NaVO_3$ and Cl_2 from NaCl and V_2O_5 in the presence of oxygen. *Ind. Eng. Chem. Res.* **2001**, *40*, 731−735.
(5) Trypuć, M.; Białowicz, K.; Kiełkowska, U. The investigations on the synthesis of $NaVO_3$ and Cl_2 from NaCl and V_2O_5 in the presence of oxygen. *Zesz. Nauk. Politech. Śląskiej* **2001**, *142*, 209−211.
(6) Trypuć, M.; Torski, Z. Conversion rate of NaCl into $NaVO_3$ in the presence of V_2O_5 and steam. *Pol. J. Appl. Chem.* **1996**, *3*, 301−306.
(7) Trypuć, M.; Torski, Z. The investigations on the synthesis of $NaVO_3$ and HCl from NaCl and V_2O_5 in the presence of steam. *Przem. Chem.* **1997**, *7*, 319−320.
(8) Trypuć, M.; Torski, Z. Investigations on the optimum conditions of NaCl conversion into $NaVO_3$. *Ind. Eng. Chem. Res.* **1998**, *37*, 1095−1098.
(9) Trypuć, M.; Białowicz, K.; Kiełkowska, U.; Torski, Z.; Mazurek, K. Synthesis of KVO_3 from KCl and V_2O_5 in the presence of oxygen. *Pol. J. Chem. Techn.* **2001**, *3*, 32−33.
(10) Trypuć, M.; Torski, Z.; Kiełkowska, U. Experimental determination of the optimum conditions of KVO_3 synthesis based on KCl and V_2O_5 in the presence of steam. *Ind. Eng. Chem. Res.* **2001**, *4*, 1022−1025.
(11) Trypuć, M.; Torski, Z.; Białowicz, K. Investigations of the influence of silicon dioxide introduced as neutral carrier on V_2O_5 conversion into KVO_3. *Pol. J. Chem. Techn.* **2001**, *3*, 28−31.
(12) Trypuć, M.; Kiełkowska, U. The investigations on $NaVO_3-NaHCO_3-H_2O$ system. *Pol. J. Appl. Chem.* **1995**, *1*, 103−109.
(13) Trypuć, M.; Kiełkowska, U. Solubility in the $NH_4HCO_3 + NH_4VO_3 + H_2O$ system. *J. Chem. Eng. Data* **1996**, *41*, 1005−1007.
(14) Trypuć, M.; Kiełkowska, U. Solubility in the $NaVO_3 + NH_4VO_3 + H_2O$ system. *J. Chem. Eng. Data* **1997**, *42*, 523−525.
(15) Trypuć, M.; Kiełkowska, U. Solubility in the $NH_4HCO_3 + NaHCO_3 + H_2O$ system. *J. Chem. Eng. Data* **1998**, *43*, 201−204.
(16) Trypuć, M.; Stefanowicz, D. Solubility in the $KVO_3-NH_4VO_3-H_2O$ system. *J. Chem. Eng. Data* **1997**, *42*, 1140−1144.
(17) Trypuć, M.; Kiełkowska, U.; Stefanowicz, D. Solubility investigations in the $KHCO_3 + NH_4HCO_3 + H_2O$ system. *J. Chem. Eng. Data* **2001**, *46*, 800 − 804.
(18) Trypuć, M.; Kiełkowska, U. Solubility diagram for the system $KHCO_3 + KVO_3 + H_2O$ at 293−323 K. *Fluid Phase Equilib.* **2003**, *213*, 81−88.
(19) Trypuć, M.; Białowicz, K. Solubility in the system $NaVO_3 + NH_4VO_3 + NH_3 + H_2O$ from 293 to 323 K. *J. Chem. Eng. Data* **2000**, *45*, 492−494.
(20) Praca zbiorowa. *Kwas siarkowy na progu integracji europejskiej*; Wydawnictwo Instytutu Ochrony Roœlin: Poznañ, 2001.
(21) Anioł, S.; Karolewicz, T.; Kubała, J. Recovery of V_2O_5 from the spent vanadium catalysts. *Pol. J. Appl. Chem.* **1997**, *41*, 25−31.
(22) Minczewski, J.; Marczenko, Z. *Chemia Analityczna*; PWN: Warszawa, 1987.
(23) Kryœciak, J. *Chemiczna Analiza Iloœciowa*; PZWL: Warszawa, 1999.
(24) Williams, W. J. *Oznaczanie Anionów*; PWN: Warszawa, 1985.
(25) Sandell, G. *Colorimetric Metal Analysis*; Interscience Publisher: New York, 1959.
(26) Sammour, H. M.; Sheglila, A. T.; Aly, F. L. *Analyst* **1997**, *102*, 180.
(27) Powder Difraction File. International Center for Diffraction Data: USA, 2001.
(28) Przybora, E. *Rentgenostrukturalne metody identyfikacji minerałów i skał*; WG: Warszawa, 1957.
(29) Broul, M.; Nyvlt, J.; Sohnel, O. *Solubility in Inorganic Two-Component Systems*; Academia: Prague, 1981.

Received for review June 17, 2005. Accepted November 23, 2005.

JE050233B