Solubility Investigations in the $KHCO_3 + NH_4HCO_3 + H_2O$ System

Mieczysław Trypuć,* Urszula Kiełkowska, and Dorota Stefanowicz

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

The mutual solubility of $KHCO_3$ and NH_4HCO_3 in water within the temperature range 293 K to 323 K was determined. From these results, a polytherm section for the $KHCO_3 + NH_4HCO_3 + H_2O$ system was plotted. Additionally, the density dependence versus the salt concentration expressed in mole fractions is presented.

Introduction

The new concept of a potassium carbonate production method based on potassium chloride and vanadium(V) oxide is being currently investigated.[1,2] The proposed model is based on potassium metavanadate as an intermediate reactant, which is subsequently transformed by several unit processes into the final product, potassium carbonate. One of the important steps of the method is the preparation of the saturated KVO_3 ammonia brine and its following carbonization to reach the designated carbonization degree (R) of the system and the maximum yield toward the ammonium ion ($W_{NH_4^+}$).

The carbonization degree of a solution (R) is defined as the relationship of CO_2 concentration in the form of HCO_3^- ions to solution alkalinity. The reaction yield toward the ammonium ions ($W_{NH_4^+}$) is described by the amount of NH_4VO_3 precipitate.

The preceding processes can be illustrated with the following reaction equations:

$$KVO_3 + NH_3 + CO_2 + H_2O \leftrightarrow NH_4VO_3\downarrow + KHCO_3 \quad (1)$$

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

A sparingly soluble precipitate of ammonium metavanadate is obtained (solubility of NH_4VO_3 at 293 K: 0.050 $mol\cdot dm^{-3}$), whereas a mixture of $KHCO_3$ and K_2CO_3 salts remains in solution, influenced by the carbonization degree (R) of the solution.

A detailed knowledge of the solubility isotherms for the $KVO_3 + NH_4HCO_3 + NH_4VO_3 + KHCO_3 + H_2O$ system is essential for an assessment of the optimum operating parameters of reactions 1 and 2. These isotherms are commonly presented in a graphic form as the projection on a plane, according to Jänecke,[3] which determines the location and dimension of the salt cocrystallization regions and the isothermal invariant points existing in the studied system.

That diagram with the plotted isohydres enables the composition determination of KVO_3 ammonia brine in the crystallization region of NH_4VO_3 with the designated parameters $W_{NH_4^+}$ and R. These calculated values are essential for the proceeding of the experimental carbonization process. The presence of plotted isodensity curves gives grounds for the calculation of NH_4VO_3 solids, equilibrium solution, and amount of water in equilibrium solution when the carbonization process is terminated.

Knowledge of mutual solubility data in four three-component systems is demanded for the presentation of the equilibrium diagram of the reciprocal salt system $KVO_3 + NH_4HCO_3 + H_2O$; i.e.,

$$NH_4HCO_3 + NH_4VO_3 + H_2O \qquad \text{(ref 4)}$$

$$KVO_3 + NH_4VO_3 + H_2O \qquad \text{(ref 2)}$$

$$KHCO_3 + NH_4HCO_3 + H_2O$$

$$KVO_3 + KHCO_3 + H_2O.$$

Each of the above-mentioned systems is located on a separate side of the diagram square in the projection of the plane. The eutonic points of the adequate three-component systems are the beginning points of lines separating off the salt crystallization regions.

Experimental results on the $NH_4HCO_3 + NH_4VO_3 + H_2O$ and $KVO_3 + NH_4VO_3 + H_2O$ systems have been recently reported by Trypuć and Kiełkowska[4] and Trypuć and Stefanowicz.[2]

The present article is a continuation of the previously undertaken project and deals with the $NH_4HCO_3 + KHCO_3 + H_2O$ system. The chosen temperature range varied from 293 K to 323 K and is consistent with those of the previously published papers.[2, 4]

Only fragmentary solubility data for the $KHCO_3 + NH_4HCO_3 + H_2O$ system at 293 K have been found, reported by Luther and Leubner.[5] The solubilities of potassium bicarbonate and ammonium bicarbonate expressed in moles per 1000 mol of H_2O at the eutonic point are presented, and they are 53.5 for $KHCO_3$ and 34.3 for NH_4HCO_3, respectively.

A literature data review concerning NH_4HCO_3 solubility in water is also presented in a previous paper by the authors.[6]

Solubility data in the two-component system of $KHCO_3 + H_2O$ from 273 K to 343 K are cited on the basis of several authors.[7] But most of the discussed papers do not investigate the operating parameters of processing or solution densities.

It should be pointed out that each of salts existing in the studied system is chemically unstable and decomposes with a temperature increase. Therefore, experiments are

---

* To whom correspondence should be addressed. E-mail: ulak@chem.uni.torun.pl.

10.1021/je0003804 CCC: $20.00

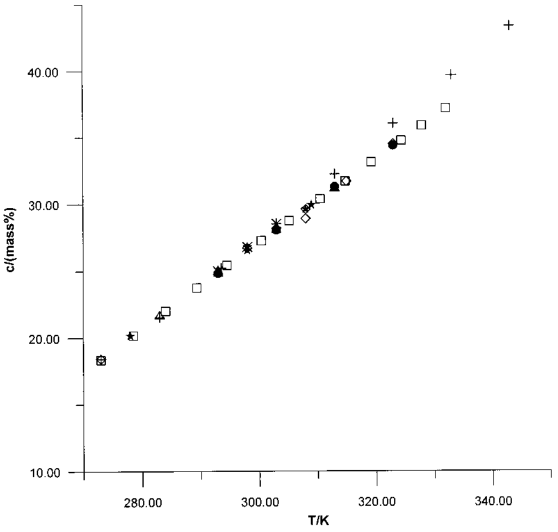

Figure 1. Literature data of the potassium bicarbonate + water system over the temperature range from 273 K to 343 K: (×) Oglesby, 1929; (◇) Krat, 1935 (273 K); Bogojawlensky, 1953, 1959 (298 K); Teeple, 1929 (308 K); Raszkowskaja, 1958 (308 K); Starkowa, 1931 (315 K); Luznaja, 1954, 1955, 1956 (315 K); (□) Dibbits, 1874; (△) Paris, 1938; (+) Takahashi, 1927; (★) Hill, 1927, 1930; (●) this work.

carried out under such pressure conditions to prevent salt decomposition. The pressure value is limited by temperature and the location of the chosen experimental point on the respective isotherm.

Experimental Section

Reagents. All chemicals used were of analytical purity grade, that is, $KHCO_3$ and NH_4HCO_3 (purity of 99.98%, POCh Gliwice S. A., Poland).

Experimental Procedure. The mutual salt solubility in the title system at 293 K, 303 K, 313 K, and 323 K was examined by the method of the isothermal solution saturation.

Sample solutions were recarbonized with gaseous CO_2. Salts existing in the studied system are chemically unstable. A technique of recarbonization was introduced to reach about 95% of the solution carbonization degree for the studied temperature range. The solution carbonization degree equals 100% at temperatures above 313 K, and 323 K can be reached when additional CO_2 pressure exceeding 10 bar is introduced. Such pressure conditions produced in a glass apparatus are dangerous and cause difficulties with the solution density determination. Previously reported data reveal that the HCO_3^- ion concentration changes only insignificantly with the increase of R above 95%.[8]

To reach an R value of 100%, data were extrapolated, but the observed concentration changes were rather small and therefore neglected.

Gaseous CO_2 introduced into the system was a protective medium against salt decomposition. The influence of CO_2 pressure on the salt solubility was not investigated. The solubility of CO_2 in saturated salt solutions especially at higher temperatures is insignificant and can be omitted in comparison to the HCO_3^- ion concentration detected in solution.

Branches I (Figure 2) of the solubility isotherms were plotted on the basis of chemical analysis of equilibrium solutions, where $KHCO_3$ was detected in the solid phase with increasing concentration of NH_4HCO_3 toward the eutonic points (E).

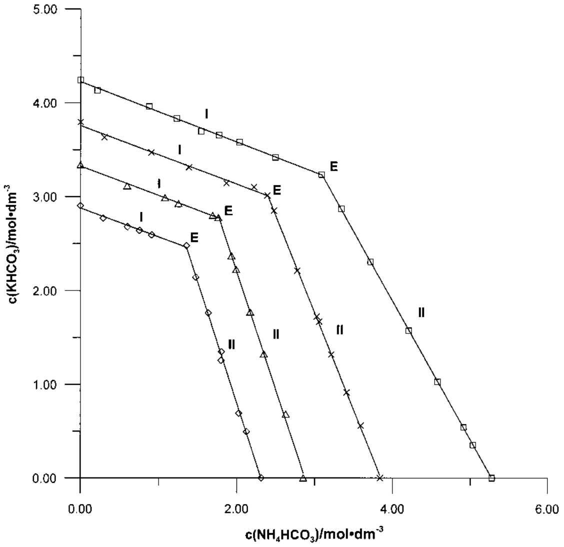

Figure 2. Solubility of $KHCO_3$ and NH_4HCO_3 in the system $KHCO_3 + NH_4HCO_3 + H_2O$: (◇) $T = 293$ K; (△) $T = 303$ K; (×) $T = 313$ K; (□) $T = 323$ K.

Branches II (Figure 2) of the solubility isotherms refer to solutions in equilibrium with the NH_4HCO_3 solids with increasing concentration of $KHCO_3$ toward the eutonic points (E).

Experiments at the temperatures 293 K and 303 K were carried out in a glass pressure apparatus described in detail in former papers.[6,8] At the temperatures 313 K and 323 K the measurements were carried out in a specially constructed pressure apparatus described in detail in the former paper.[8] Pressure control was performed using a manometer, and the determination precision was evaluated to be ±0.1 bar.

At temperatures of 293 K and 303 K, the determinations were performed with p_{CO_2} of about 2 bar whereas, at 313 K and 323 K, p_{CO_2} was varied from 3.5 bar to 5 bar, depending upon the isotherm location of the chosen experimental point.

Solutions with a stated excess of the solid phase were placed in a thermostated bath for a period of 12 h with continuous electromagnetic stirring. This procedure enabled the state of equilibrium between solution and the solid phase.

The constant temperature was kept using Polystat CC1 (Germany) with the determination precision ±0.02 K.

After the fixed time limit, stirring was discontinued to sediment the solids. The clear equilibrium solution was sampled into two calibrated Ostwalds' pycnometers under adjusted equilibrium pressure, protecting the gaseous phase bubbles that appear. Each sample was in the compressed liquid state. The laboratory technique was described in detail in a former paper.[8]

The overall content of the first pycnometer was employed for the solution density determination with the precision ± 0.002 g·cm^{-3}. Next, the sample solution was transferred quantitatively to the graduated flask and diluted, and the ammonium, potassium, and HCO_3^- ion analysis was performed.

The other pycnometer's content was employed for the determination of CO_2 concentration in solution. The overall concentration of CO_2 was measured in a specially built apparatus.[8,12] The CO_2 concentration determination was used for the assessment of solution carbonization degree (R).

Analytical Methods. The potassium ion concentration was measured by a weighing method in the form of potassium tetraphenyloborate ($K[B(C_6H_5)_4]$) under the acidic conditions of 2 M HCl.[8,9] Solids precipitated out under the acidic conditions are coarse-crystalline and therefore easier to handle for the filtration procedure. NH_4^+ ion species were removed out of solution using a heated solution of 0.5 M NaOH. Next, 2 M HCl was applied. Potassium ions were precipitated out using sodium tetraphenyloborate solution in 0.01 M NaOH. Solids were filtered out using the melting crucible with a porous bottom and then rinsed with the prepared solution consisting of sodium tetraphenyloborate in acetic acid and distilled water. Precipitates were dried to constant mass at the temperature 378 K.

The average relative error of the measurement was estimated to be ±1.5%.

The NH_4^+ ion concentration was evaluated employing the distillation method,[11] using a fully automatic distillation apparatus Vapodest 30 (Gerhardt, Germany). Ammonia was desorbed out of solution using strong base and then adsorbed with a titer sulfuric acid solution. The remaining excess of acid was potentiometrically titrated with a titer NaOH solution. The average relative error was estimated to be ±1%.

The HCO_3^- ion concentration was determined by a method of potentiometric titration applying 0.1 M HCl.[10,11] An automatic titrator 716 DMS was employed with a combined glass electrode supplied by Metrohm, Switzerland. The average relative error was estimated to be less than 1%.

Identification of Solid Phases. A HZG 4/A-2 X-ray diffraction analyzer (Germany) with continuous registration was used for solid-phase X-ray diffraction analysis. Wet crystals were analyzed directly after the equilibrium solution was filtered out. This procedure enabled a certain determination of the solid-phase composition in equilibrium with the solutions. The solid phase was dried at room temperature, pestled into a powder, and then analyzed by X-ray diffraction.

The X-ray analyses of the solid phases were based on the distribution curves of the dispersed radiation intensity $I = f(\theta)$. For the quantitative analysis, each of the diffraction patterns was inspected for the series of interplanar distance (d) and relative intensity (I) and then compared with the numeric data listed in “The powder diffraction file”.[13]

Results and Conclusions

Literature data comparisons for the discussed two-component system $KHCO_3 + H_2O$[14−28] within the inspected temperature range 293 K to 323 K with the obtained experimental data are tabulated in Table 1.

Solubility data of potassium bicarbonate in water within 273 K to 343 K measured by various cited authors are plotted in Figure 1. These results are expressed in mass fraction. The experimental values of $KHCO_3$ concentration are in good correlation with the cited data.

A literature data review for the $NH_4HCO_3 + H_2O$ system has been reported previously.[6]

Experimental results of the mutual solubility of $KHCO_3$ and NH_4HCO_3 salts in water are collected in Table 2.

The solution density (ρ) is given in kilograms per cubic meter, the ion concentration values (c) are expressed both in moles per cubic decimeter and in mole fraction (x). These results gave grounds for plotting a polytherm section of the $KHCO_3 + NH_4HCO_3 + H_2O$ system (Figure 2).

Table 1. Comparison of Experimental Solubility Data for the $KHCO_3 + H_2O$ System with the Literature Values over a Temperature Range 293 K to 323 K

	c/(mass %)		s/(g/100 g H_2O)	
T/K	exp	lit.	exp	lit.
293	24.82	24.98[a] 25.09[b] 25.23[c]	33.03	33.19[b]
303	28.05	28.52[a] 28.18[b] 28.52[c]	38.99	39.93[a] 39.23[b]
313	31.30	31.80[d] 31.28[b] 32.24[c]	45.55	45.51[b]
323	34.38	34.50[e] 36.04[c]	52.39	-

[a] Oglesby (1929). [b] Paris (1938). [c] Takahashi (1927) for 293.5 K. [d] Bogojawlensky (1959). [e] Luznaja (1954, 1955, 1956).

The course of branches I of the solubility isotherm for the studied temperature range is linear. The $KHCO_3$ concentration with increasing increments of concentration of NH_4HCO_3 is diminishing toward the eutonic points (E). The detected decrease is estimated to be 0.427 mol·dm^{-3} at 293 K, 0.564 mol·dm^{-3} at 303 K, 0.783 mol·dm^{-3} at 313 K, and 1.004 mol·dm^{-3} at 323 K, respectively.

Branches II of the solubility isotherms correspond with the saturated solution of NH_4HCO_3 with increasing concentration of $KHCO_3$ toward the eutonic points. The observed decrease in the NH_4HCO_3 solubility values is linked with the presence of $KHCO_3$ in solution, and the solubility is increased with the rise of temperature values, that is, 0.963 mol·dm^{-3} at $T = 293$ K, 1.094 mol·dm^{-3} at $T = 303$ K, 1.451 mol·dm^{-3} at $T = 313$ K, and 2.192 mol·dm^{-3} at $T = 323$ K, respectively.

The specific course of the respective solubility isotherms (Figure 1) implies that the solubility values of $KHCO_3$ and NH_4HCO_3 are increased with the temperature rise. The $KHCO_3$ concentration is increased systematically with temperature and at $T = 323$ K is about 46% higher than that at $T = 293$ K. In comparison, the NH_4HCO_3 concentration is 127% higher under the same processing conditions. This fact implies that the temperature influence on the ammonium bicarbonate solubility is more strongly marked than that of potassium bicarbonate.

The calculated salt concentrations of $KHCO_3$ and NH_4HCO_3 at the eutonic point at $T = 293$ K are given: 54.02 and 29.53 mol per 1000 mol of H_2O, respectively. The reported former concentration values are 53.5 for $KHCO_3$ and 34.3 for NH_4HCO_3, respectively.[5]

The detected discrepancies in the concentration values between the cited literature and experimental results can be linked with the salts’ chemical instability. The authors[5] do not present the description of experimental conditions or solution densities. This inconsistency may be caused by the CO_2 pressure parameter introduced into the system, which guarantees only the presence of HCO_3^- ions in solution.

The possible formation of binary salts or any other addition combination is detected employing the equilibrium diagram property—composition type.[29] When a new solid phase is created in the system, some distinctive bends or curvings in points referring to the new formation are observed on curves illustrating the solution density dependence versus the salt concentration.

On the basis of data collected in Table 2, a relationship between the solution density and the salt concentration values expressed in mole fractions (Figure 3) was found.

Table 2. Solubility in the System $KHCO_3$ (1) + NH_4HCO_3 (2) + H_2O (3)

ρ/kg·m^{-3}	c_1^{a}	c_2^{a}	x_1^{a}	x_2^{a}	solid phase
			T = 293 K		
1.171	2.904	0.000	1.000	0.000	$KHCO_3$
1.173	2.769	0.289	0.905	0.095	$KHCO_3$
1.175	2.679	0.599	0.817	0.183	$KHCO_3$
1.176	2.639	0.751	0.778	0.222	$KHCO_3$
1.178	2.592	0.907	0.741	0.259	$KHCO_3$
1.181	2.477	1.354	0.647	0.353	NH_4HCO_3, $KHCO_3$
1.163	2.143	1.471	0.593	0.407	NH_4HCO_3
1.138	1.760	1.633	0.519	0.481	NH_4HCO_3
1.120	1.347	1.801	0.428	0.572	NH_4HCO_3
1.118	1.252	1.796	0.411	0.589	NH_4HCO_3
1.094	0.691	2.023	0.255	0.745	NH_4HCO_3
1.086	0.495	2.124	0.189	0.811	NH_4HCO_3
1.072	0.000	2.317	0.000	1.000	NH_4HCO_3
			T = 303 K		
1.192	3.340	0.000	1.000	0.000	$KHCO_3$
1.195	3.115	0.594	0.840	0.160	$KHCO_3$
1.198	2.988	1.078	0.735	0.265	$KHCO_3$
1.198	2.926	1.249	0.701	0.299	$KHCO_3$
1.201	2.800	1.689	0.624	0.376	$KHCO_3$
1.202	2.776	1.760	0.612	0.388	NH_4HCO_3, $KHCO_3$
1.177	2.370	1.929	0.551	0.449	NH_4HCO_3
1.171	2.227	1.990	0.528	0.472	NH_4HCO_3
1.151	1.772	2.169	0.450	0.550	NH_4HCO_3
1.127	1.324	2.345	0.361	0.639	NH_4HCO_3
1.102	0.681	2.628	0.206	0.794	NH_4HCO_3
1.094	0.000	2.854	0.000	1.000	NH_4HCO_3
			T = 313 K		
1.214	3.795	0.000	1.000	0.000	$KHCO_3$
1.215	3.631	0.305	0.923	0.077	$KHCO_3$
1.216	3.471	0.902	0.794	0.206	$KHCO_3$
1.218	3.313	1.381	0.706	0.294	$KHCO_3$
1.220	3.143	1.862	0.628	0.372	$KHCO_3$
1.222	3.101	2.216	0.583	0.417	$KHCO_3$
1.223	3.012	2.388	0.558	0.442	NH_4HCO_3, $KHCO_3$
1.215	2.849	2.473	0.535	0.465	NH_4HCO_3
1.185	2.211	2.771	0.444	0.556	NH_4HCO_3
1.164	1.723	3.023	0.363	0.637	NH_4HCO_3
1.161	1.670	3.054	0.354	0.646	NH_4HCO_3
1.151	1.318	3.209	0.291	0.709	NH_4HCO_3
1.140	0.912	3.409	0.211	0.789	NH_4HCO_3
1.128	0.561	3.591	0.135	0.865	NH_4HCO_3
1.116	0.000	3.839	0.000	1.000	NH_4HCO_3
			T = 323 K		
1.235	4.241	0.000	1.000	0.000	$KHCO_3$
1.236	4.133	0.214	0.951	0.049	$KHCO_3$
1.236	3.961	0.873	0.819	0.181	$KHCO_3$
1.237	3.835	1.226	0.758	0.242	$KHCO_3$
1.237	3.696	1.541	0.706	0.294	$KHCO_3$
1.238	3.657	1.768	0.674	0.326	$KHCO_3$
1.238	3.581	2.032	0.638	0.362	$KHCO_3$
1.239	3.420	2.490	0.579	0.421	$KHCO_3$
1.240	3.237	3.085	0.512	0.488	NH_4HCO_3, $KHCO_3$
1.216	2.870	3.341	0.462	0.538	NH_4HCO_3
1.199	2.307	3.715	0.383	0.617	NH_4HCO_3
1.176	1.575	4.206	0.272	0.728	NH_4HCO_3
1.159	1.028	4.578	0.183	0.817	NH_4HCO_3
1.151	0.541	4.913	0.099	0.901	NH_4HCO_3
1.144	0.354	5.034	0.066	0.934	NH_4HCO_3
1.138	0.000	5.277	0.000	1.000	NH_4HCO_3

[a] In mol·dm^{-3}.

The solution density values are increased slightly with the rise of NH_4HCO_3 concentration (for the saturated solutions of $KHCO_3$), reaching the maximum values at the eutonic points E. When these specific points are exceeded, the density values are decreased and reach the similar values of NH_4HCO_3 saturated solutions. The monotonic course of the curves implies that no chemical compound is formed in the studied system.

An X-ray analysis of the solids and the specific course of the curves plotted in Figure 3 point out clearly that within the examined temperature range the solid phase is composed of $KHCO_3$ (branch I), NH_4HCO_3 (branch II), and the mixture of those two salts existing at the eutonic points (E).

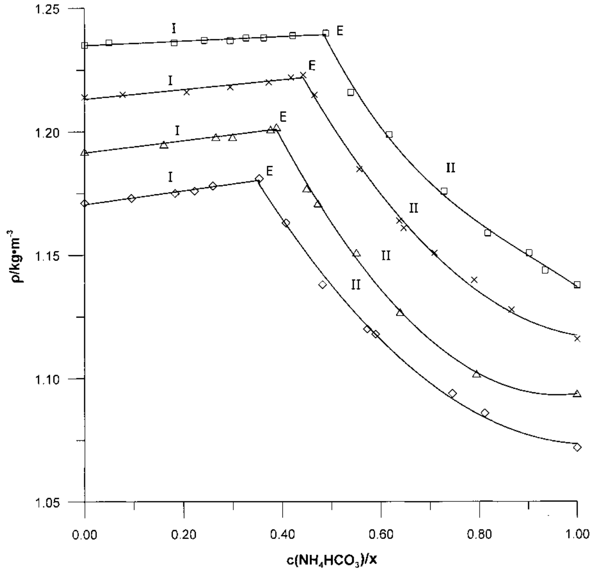

Figure 3. Density–mole fraction relationships of NH_4HCO_3 in the $KHCO_3$ + NH_4HCO_3 + H_2O system: (◇) T = 293 K; (△) T = 303 K; (×) T = 313 K; (□) T = 323 K.

Literature Cited

(1) 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.
(2) Trypuć, M.; Stefanowicz, D. I. Solubility in the KVO_3 + NH_4VO_3 + H_2O system. *J. Chem. Eng. Data* **1997**, *42*, 1140–1144.
(3) Wiktorow, M. M. *Obliczenia graficzne w technologii substancji nieorganicznych*; WNT: Warsaw, Poland, 1975.
(4) Trypuć, M.; Kiełkowska, U. Solubility in the NH_4HCO_3 + NH_4VO_3 + H_2O system. *J. Chem. Eng. Data* **1996**, *41*, 1005–1007.
(5) Luther, R.; Leubner, H. *Z. Naturforsch.* **1951**, *6a*, 385 (cited in Pelsh, 1961).
(6) Trypuć, M.; Kiełkowska, U. Solubility in the NH_4HCO_3 + $NaHCO_3$ + H_2O System. *J. Chem. Eng. Data* **1998**, *43*, 201–204.
(7) Pelsh, A. D. *Spravotschnik po Rastvorimosti Solyevykh System*; Nauka, Goskchimisdat: Leningrad, Russia, 1961.
(8) Trypuć, M.; Kiełkowska, U. Solubility in the $NaVO_3$ + NH_4HCO_3 + NH_4VO_3 + $NaHCO_3$ + H_2O system. *Pol. J. Chem. Technol.* **1999**, *1*, 40–44.
(9) Furman, N. H. *Standard method of chemical analysis*; D. Van Nostrand Co.: Princeton, NJ, 1962; Vol. I.
(10) Minczewski, J.; Marczenko, Z. *Chemia analityczna*; PWN: Warsaw, Poland, 1987.
(11) Struszyński, M. *Analiza iloóciowa i techniczna*; PWT: Warsaw, Poland, 1954.
(12) Koneczny, H.; Trypuć, M.; Gulewicz, K. Oznaczanie CO_2 w produktach przemysłu sodowego. *Przem. Chem.* **1964**, *12*, 691–692.
(13) *Powder Diffraction File*; Joint Committee on Powder Diffraction Standards: New Jersey, 1976.
(14) Bogojawlensky, P. S.; Manannikoa, A. S. *Sb. Tr. Losk. GW-Z Inst.* **1953**, *6*, 378 (cited in Pelsh, 1961).
(15) Bogojawlensky, P. S.; et al. *Sci. Sin.* **1959**, *8*, 580 (cited in Pelsh, 1961).
(16) Dibbits, H. C. *J. Prakt. Chem.* **1874**, *10*, 429 (cited in Pelsh, 1961).
(17) Hill, A. E. *J. Am. Chem. Soc.* **1927**, *49*, 968 (cited in Pelsh, 1961).
(18) Hill, A. E. *J. Am. Chem. Soc.* **1930**, *52*, 3819 (cited in Pelsh, 1961).
(19) Krat, W. N.; Kosiaczkowa, S. N. *Izv. SFChA Akad. Nauk SSSR* **1954**, *25*, 347 (cited in Pelsh, 1961).
(20) Luznaja, N. P.; Kosiaczkowa, S. N. *Izv. SFChA Akad. Nauk SSSR* **1954**, *25*, 347 (cited in Pelsh, 1961).
(21) Luznaja, N. P.; Kosiaczkowa, S. N. *Izv. SFChA Akad. Nauk SSSR* **1955**, *26*, 261 (cited in Pelsh, 1961).
(22) Luznaja, N. P.; Kosiaczkowa, S. N. *Izv. SFChA Akad. Nauk SSSR* **1956**, *27*, 360 (cited in Pelsh, 1961).
(23) Oglebsy, N. E. *J. Am. Chem. Soc.* **1929**, *51*, 2356 (cited in Pelsh, 1961).

(24) Paris, R.; Mondain-Manal, P. *Bull. Soc. Chim. Fr.* **1938**, *5*, 1146 (cited in Pelsh, 1961).
(25) Raszkowskaja, E. A.; Averbah, S. N.; et al. *Ukr. Khim. Z.* **1958**, *24*, 512 (cited in Pelsh, 1961).
(26) Starkowa, Z. P. *Z. Obsch. Khim*. **1931**, *1*, 749 (cited in Pelsh, 1961).
(27) Takahashi, G. *Bull. Imp. Hyg. Lab. (Tokyo)* **1927**, *29*, 165 (cited in Pelsh, 1961).
(28) Teeple, J. E. *The Industrial Deelopment of Searles Lakes Brines;* 1929; p 132 (cited in Pelsh, 1961).
(29) Sułajmankułov, K. *Sojedinienia karbamida s nieorganitscheskimi soliami*; ILIM: Frunze, Russia 1971.

Received for review December 13, 2000. Accepted February 27, 2001. This work was supported by Grant KBN No. 3 T09 B 04218 from Komitet Badań Naukowych (State Committee for Scientific Research).

JE0003804