JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

ARTICLE

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Solubility in the Reciprocal Quaternary $NH_4^+-Na^+-NO_3^--VO_3^--H_2O$ System at (313 and 323) K

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ABSTRACT: The equilibrium solubility studies of the $NH_4NO_3 + NaVO_3 + H_2O$ system at (313 and 323) K have been performed. On the basis of the results, the equilibrium plots for the system in a planar projection have been obtained according to the Jänecke method. The plots enable the determination of the optimal conditions for the conversion reaction of ammonium nitrate into sodium nitrate with the use of sodium metavanadate. The source of ammonium nitrate is the postfiltration lye from the soda production with the soda−chlorine−saltpeter (SCS) method. The conversion of NH_4NO_3 from the postfiltration lye into $NaNO_3$ cancels the risk of explosion during the process of production of ammonium−sodium saltpeter.

INTRODUCTION

Sodium carbonate is one of the basic products of the inorganic industry. That compound is used among others as a flux agent in a process of glass production or as a substrate for production of water glass.[1,2] The production of sodium carbonate reaches ca. 50 million ton per year, and about 50 % of that is produced with the Solvay method. That method is based on the easily available raw materials such as halite, limestone, carbon, and ammonia.[3,4] That technology is characterized by the significant noxiousness for the natural environment, mainly due to the emission of large amounts of the liquid waste ($CaCl_2$ and NaCl solution) and solid waste ($CaCO_3$, $Ca(OH)_2$, ashes).[3,4]

An alternative method of sodium carbonate production which relies on the same raw materials is the wasteless soda−chlorine−saltpeter (SCS) method. The difference between SCS and the Solvay method is that during the carbonization process (eq 1) the sodium nitrate brine is used instead of sodium chloride. Sodium nitrate is obtained in the process of oxidation of solid sodium chloride with the nitric acid in the presence of air. The second valuable product in that process is chlorine.[4,5]

$$NaNO_3 + NH_3 + CO_2 + H_2O \leftrightarrow NaHCO_3\downarrow + NH_4NO_3 \quad (1)$$

The solution obtained after filtration of sodium bicarbonate contains mainly ammonium nitrate, unreacted sodium nitrate, and a small amount of sodium chloride. The obtained lye is used in the production of mixed ammonium−sodium saltpeter, which is further used as a fertilizer. The transformation of that saltpeter into the nitrogenous fertilizer is difficult because of the presence of chloride ions and explosive properties of ammonium nitrate. Chloride ions catalyze the decomposition of ammonium nitrate, which causes the loss of nitrogen during the production and real risk of explosion during the processes of concentration, crystallization, and storage of the produced ammonium−sodium saltpeter.[5−7]

This phenomenon can be eliminated by modification of the SCS method based on the conversion of ammonium nitrate into sodium nitrate with sodium metavanadate (eq 2). The solution of sodium nitrate obtained in that process does not cause any risk of explosion during the production of sodium saltpeter.[8,9]

$$NH_4NO_3 + NaVO_3 \leftrightarrow NH_4VO_3\downarrow + NaNO_3 \quad (2)$$

The precipitated ammonium metavanadate is subjected to calcination (eq 3), to recover ammonia and vanadium(V) oxide, which in turn is used to synthesize sodium metavanadate (eq 4).

$$2NH_4VO_3 \rightarrow 2NH_3 + V_2O_5 + H_2O \quad (3)$$

$$V_2O_5 + 2NaCl + 1/2O_2 \rightarrow 2NaVO_3 + Cl_2 \quad (4)$$

The chemical flow diagram of the proposed modification of the SCS method can be found in our previous papers.[8−10,14]

The conversion process mentioned above (eq 2) is a reaction of double ion exchange in the water medium, and the factors determining the equilibrium of that reaction are the mutual solubility of the system components and temperature. The detailed knowledge of the investigated system, that is, the qualitative and qualitative relationships, requires the detailed equilibrium research of the mutual solubility of salts for the pairs of exchanging salts $NH_4NO_3 + NaVO_3 + H_2O$ and for four ternary subsystems $NaNO_3 + NaVO_3 + H_2O$, $NH_4NO_3 + NH_4VO_3 + H_2O$, $NaNO_3 + NH_4NO_3 + H_2O$, and $NaVO_3 + NH_4VO_3 + H_2O$. Data for the ternary subsystems have been published previously;[10−13] some data on the quaternary system can be found in literature.[14,15] The obtained experimental data enable us to build the equilibrium plots for the investigated system of pairs of the exchange salts, which are required for determination of the process parameters such as temperature, composition of the brine subjected to conversion, and the process yield.

EXPERIMENTAL SECTION

Equipment and Reagents. Research was conducted with the water thermostat Polystat CC1 of a precision ± 0.02 K, and the

Received: February 4, 2011
Accepted: April 29, 2011
Published: May 10, 2011

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Table 1. Composition of the Equilibrium Solutions and the Solid Phase for the $NaVO_3 + NH_4NO_3 + NaNO_3 + NH_4VO_3 + H_2O$ System at 313 K

d	pH	*c* (mol·dm^{-3})				mole fraction		solid phase
g·cm^{-3}		Na^+	NH_4^+	V(V)	NO_3^-	V(V)	Na^+	
				Branch E_1-P_2				
1.337	4.31	0	12.116	$9.6 \cdot 10^{-5}$	12.116	$8 \cdot 10^{-6}$	0	NH_4NO_3, NH_4VO_3
1.359	4.33	0.610	11.814	$9.8 \cdot 10^{-5}$	12.424	$8 \cdot 10^{-6}$	0.049	NH_4NO_3, NH_4VO_3
1.382	4.32	1.316	11.437	$9.9 \cdot 10^{-5}$	12.753	$8 \cdot 10^{-6}$	0.103	NH_4NO_3, NH_4VO_3
1.408	4.33	2.100	11.075	$9.9 \cdot 10^{-5}$	13.174	$8 \cdot 10^{-6}$	0.159	NH_4NO_3, NH_4VO_3
1.426	4.34	2.565	10.838	$9.9 \cdot 10^{-5}$	13.403	$8 \cdot 10^{-6}$	0.191	NH_4NO_3, NH_4VO_3
1.460	4.16	3.478	10.461	$9.9 \cdot 10^{-5}$	13.939	$8 \cdot 10^{-6}$	0.250	NH_4NO_3,NH_4VO_3, $NaNO_3$
				Branch P_1-P_2				
1.460	4.16	3.478	10.461	$9.9 \cdot 10^{-5}$	13.939	$8 \cdot 10^{-6}$	0.250	NH_4NO_3, NH_4VO_3, $NaNO_3$
1.442	4.31	4.236	8.409	$1.00 \cdot 10^{-4}$	12.645	$8 \cdot 10^{-6}$	0.335	NH_4VO_3, $NaNO_3$
1.431	4.97	4.942	6.611	$1.14 \cdot 10^{-4}$	11.553	$1.0 \cdot 10^{-5}$	0.428	NH_4VO_3, $NaNO_3$
1.425	4.62	5.584	5.024	$1.23 \cdot 10^{-4}$	10.608	$1.2 \cdot 10^{-5}$	0.526	NH_4VO_3, $NaNO_3$
1.418	4.77	6.156	3.615	$1.51 \cdot 10^{-4}$	9.771	$1.5 \cdot 10^{-5}$	0.630	NH_4VO_3, $NaNO_3$
1.415	4.95	7.156	2.376	$1.71 \cdot 10^{-4}$	9.532	$1.8 \cdot 10^{-5}$	0.751	NH_4VO_3, $NaNO_3$
1.412	5.34	7.619	1.333	$6.52 \cdot 10^{-4}$	8.951	$7.3 \cdot 10^{-5}$	0.851	NH_4VO_3, $NaNO_3$
1.411	5.65	7.955	0.876	0.0032	8.827	$3.66 \cdot 10^{-4}$	0.901	NH_4VO_3, $NaNO_3$
1.411	6.16	8.072	0.702	0.0060	8.767	$6.79 \cdot 10^{-4}$	0.920	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, NH_4VO_3, $NaNO_3$
				Branch P_1-E_2				
1.411	6.16	8.072	0.702	0.0060	8.767	$6.79 \cdot 10^{-4}$	0.920	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, NH_4VO_3, $NaNO_3$
1.346	6.35	6.564	0.580	0.017	7.126	0.0024	0.919	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, NH_4VO_3
1.280	6.37	5.323	0.511	0.040	5.793	0.0069	0.913	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, NH_4VO_3
1.212	6.46	3.896	0.440	0.200	4.136	0.0461	0.899	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, NH_4VO_3
1.123	6.62	2.116	0.332	0.334	2.114	0.1364	0.864	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, NH_4VO_3
1.125	6.90	1.733	0.335	0.960	1.108	0.4643	0.838	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, NH_4VO_3
1.155	7.02	1.865	0.395	1.612	0.649	0.7130	0.825	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, NH_4VO_3
1.174	7.14	1.915	0.410	2.055	0.270	0.8837	0.824	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, NH_4VO_3
1.220	-	2.115	0.455	2.570	0	1	0.823	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, NH_4VO_3
				Branch P_1-E_3				
1.411	6.16	8.072	0.702	0.0060	8.767	$6.79 \cdot 10^{-4}$	0.920	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, NH_4VO_3, $NaNO_3$
1.409	6.20	8.140	0.448	0.0051	8.583	$5.94 \cdot 10^{-4}$	0.948	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, $NaNO_3$
1.406	6.13	8.170	0.286	0.0045	8.452	$5.32 \cdot 10^{-4}$	0.966	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, $NaNO_3$
1.407	6.52	8.234	0.140	0.0041	8.370	$4.90 \cdot 10^{-4}$	0.983	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, $NaNO_3$
1.419	7.69	8.377	0.000	0.0037	8.373	$4.46 \cdot 10^{-4}$	1	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, $NaNO_3$
				Branch P_2-E_4				
1.460	4.16	3.478	10.461	$9.9 \cdot 10^{-5}$	13.939	$8 \cdot 10^{-6}$	0.250	NH_4NO_3, NH_4VO_3, $NaNO_3$
1.468	-	3.496	10.553	0	14.049	0	0.249	NH_4NO_3, $NaNO_3$

required temperature was monitored with the mercury thermometer of a precision ± 0.1 K. The X-ray diffraction analysis of the solid phase was performed with PHILIPS X′Pert Pro. The spectrophotometric analyses were performed with the dual beam UVD-3000 LABOMED.

For the research the analytical grade reagents were used: NH_4VO_3 (purity ≥ 99 %, Aldrich), $NaVO_3$ (purity ≥ 98 %, Fluka), NH_4NO_3 (purity ≥ 99 %, POCH), and $NaNO_3$ (purity ≥ 99.5 %, POCH).

Method. The mutual solubility of salts in the investigated system was determined with the method of isothermal saturation of solutions[16,17] at (313 and 323) K. The experiment was performed with the use of the water thermostat with the magnetic stirrer.

The position of the ternary points P_1 and P_2 was determined in the first step, while the composition of eutonic solutions for the respective ternary systems was published in our previous papers.[10−13]

To determine the solution composition at P_1 and P_2 points, the required amounts of salts and the redistilled water were put into the 100 cm^3 Erlenmeyer flasks with the grinded neck. An excess of salts was used relative to their water solubility. The samples prepared as described above were thermostatted and stirred until the equilibrium between the phases was reached. The time of equilibration for the ternary points was determined experimentally for both temperatures. To achieve that, the concentration of vanadate(V) and ammonium ions was determined in

Table 2. Composition of the Equilibrium Solutions and the Solid Phase for the $NaVO_3 + NH_4NO_3 + NaNO_3 + NH_4VO_3 + H_2O$ System at 323 K

d	pH	c (mol·dm^{-3})				mole fraction		solid phase
g·cm^{-3}		Na^+	NH_4^+	V(V)	NO_3^-	V(V)	Na^+	
Branch E_1-P_2								
1.362	3.90	0	12.948	$1.78 \cdot 10^{-4}$	12.948	$1.4 \cdot 10^{-5}$	0	NH_4NO_3, NH_4VO_3
1.368	4.10	0.564	12.610	$1.72 \cdot 10^{-4}$	13.173	$1.3 \cdot 10^{-5}$	0.043	NH_4NO_3, NH_4VO_3
1.383	4.10	1.114	12.356	$1.64 \cdot 10^{-4}$	13.470	$1.2 \cdot 10^{-5}$	0.083	NH_4NO_3, NH_4VO_3
1.391	4.14	1.570	12.084	$1.60 \cdot 10^{-4}$	13.654	$1.2 \cdot 10^{-5}$	0.115	NH_4NO_3, NH_4VO_3
1.420	4.18	2.336	11.659	$1.54 \cdot 10^{-4}$	13.995	$1.1 \cdot 10^{-5}$	0.167	NH_4NO_3, NH_4VO_3
1.443	4.21	2.769	11.464	$1.53 \cdot 10^{-4}$	14.233	$1.1 \cdot 10^{-5}$	0.195	NH_4NO_3, NH_4VO_3
1.465	4.27	3.547	11.027	$1.47 \cdot 10^{-4}$	14.574	$1.0 \cdot 10^{-5}$	0.243	NH_4NO_3, NH_4VO_3, $NaNO_3$
Branch P_1-P_2								
1.465	4.27	3.547	11.027	$1.47 \cdot 10^{-4}$	14.574	$1.0 \cdot 10^{-5}$	0.243	NH_4NO_3, NH_4VO_3, $NaNO_3$
1.458	4.30	4.204	9.978	$1.47 \cdot 10^{-4}$	14.182	$1.0 \cdot 10^{-5}$	0.296	NH_4VO_3, $NaNO_3$
1.449	4.33	4.641	8.580	$1.48 \cdot 10^{-4}$	13.220	$1.1 \cdot 10^{-5}$	0.351	NH_4VO_3, $NaNO_3$
1.444	4.35	5.148	7.706	$1.49 \cdot 10^{-4}$	12.854	$1.2 \cdot 10^{-5}$	0.400	NH_4VO_3, $NaNO_3$
1.435	4.36	5.563	6.623	$1.52 \cdot 10^{-4}$	12.186	$1.2 \cdot 10^{-5}$	0.456	NH_4VO_3, $NaNO_3$
1.436	4.37	6.228	5.047	$1.54 \cdot 10^{-4}$	11.275	$1.4 \cdot 10^{-5}$	0.552	NH_4VO_3, $NaNO_3$
1.429	4.54	6.900	3.596	$1.55 \cdot 10^{-4}$	10.497	$1.5 \cdot 10^{-5}$	0.657	NH_4VO_3, $NaNO_3$
1.427	4.89	7.645	2.242	$3.26 \cdot 10^{-4}$	9.886	$3.3 \cdot 10^{-5}$	0.773	NH_4VO_3, $NaNO_3$
1.424	5.16	8.026	1.390	0.0012	9.415	$1.33 \cdot 10^{-4}$	0.852	NH_4VO_3, $NaNO_3$
1.426	5.92	8.569	0.844	0.0064	9.150	$7.03 \cdot 10^{-4}$	0.910	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, NH_4VO_3, $NaNO_3$
Branch P_1-E_2								
1.426	5.92	8.569	0.844	0.0064	9.150	$7.03 \cdot 10^{-4}$	0.910	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, NH_4VO_3, $NaNO_3$
1.383	6.25	7.598	0.555	0.019	8.134	0.0024	0.932	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, NH_4VO_3
1.325	6.27	6.401	0.525	0.041	6.885	0.0059	0.924	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, NH_4VO_3
1.267	6.28	5.208	0.449	0.095	5.563	0.0168	0.921	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, NH_4VO_3
1.225	6.30	3.200	0.406	0.358	3.248	0.0993	0.888	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, NH_4VO_3
1.162	6.32	2.914	0.396	0.386	2.924	0.1167	0.880	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, NH_4VO_3
1.121	6.62	2.283	0.387	0.731	1.938	0.2740	0.855	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, NH_4VO_3
1.132	6.88	1.996	0.392	1.312	1.075	0.5496	0.836	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, NH_4VO_3
1.182	7.26	2.047	0.454	2.023	0.478	0.8091	0.819	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, NH_4VO_3
1.262	-	2.385	0.543	2.928	0	1	0.815	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, NH_4VO_3
Branch P_1-E_3								
1.426	5.92	8.569	0.844	0.0064	9.150	$7.03 \cdot 10^{-4}$	0.910	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, NH_4VO_3, $NaNO_3$
1.423	6.25	8.606	0.470	0.0062	9.070	$6.86 \cdot 10^{-4}$	0.948	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, $NaNO_3$
1.426	6.39	8.673	0.278	0.0059	8.946	$6.60 \cdot 10^{-4}$	0.969	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, $NaNO_3$
1.426	6.62	8.750	0.137	0.0057	8.881	$6.37 \cdot 10^{-4}$	0.985	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, $NaNO_3$
1.431	6.71	8.871	0	0.0052	8.866	$5.86 \cdot 10^{-4}$	1	β-$NaVO_3$, $NaVO_3 \cdot 2H_2O$, $NaNO_3$
Branch P_2-E_4								
1.465	4.27	3.547	11.027	$1.47 \cdot 10^{-4}$	14.574	$1.0 \cdot 10^{-5}$	0.243	NH_4NO_3, NH_4VO_3, $NaNO_3$
1.484	-	3.397	11.170	0	14.567	0	0.233	NH_4NO_3, $NaNO_3$

the samples of the solution collected during the equilibration procedure. The lack of statistically significant differences between the pair of subsequent analyses was treated as an indication of the equilibrium reached between the solid phase and the solution. For both temperatures, the determined equilibration time was ∼168 h.

After reaching the equilibrium, the stirring was stopped, and the mixture was left for sedimentation. The time of sedimentation was up to 24 h. The clear equilibrated solutions were sampled into the precalibrated Ostwald flow pycnometer for the density determination. The contents of the pycnometer were quantitatively transferred into the measuring flasks and diluted with the redistilled water, and the solutions obtained in that way were subjected to the chemical analysis.

In the subsequent step of the research, the branches of the solubility isotherms were determined. The solutions were saturated with the pair of required salts, while the concentration of the third salt was varied as required for the determination of the respective branch of the isotherm. The required mixtures were prepared in the way analogous to that described for the ternary points. The samples were thermostatted at the selected temperature

Table 3. Comparison of Water Solubility of Sodium Metavanadate in the Binary System

T (K)	solubility $NaVO_3$ ($g \cdot 100\ g^{-1}\ H_2O$)		
	this work	ref 13	ref 22
293	17.40	17.71	19.59
303	21.37	20.85	22.77
313	23.70	23.83	26.08
323	26.28	27.61	29.54

and stirred for the time required for reaching the equilibrium between the phases, as determined for the ternary points.

The equilibrated solutions were used to determine the concentration of sodium ions with either the gravimetric method Kolthoff and Barber[18] or the flame photometry, and the concentration of ammonium ions was determined with either the formalin method[18] or by the distillation method together with the nitrate ions as total ammonia.[18,19] The vanadate(V) ions were determined spectrophotometrically by either the peroxide method or with the use of PAR, depending on their concentration. The details of the analytical procedure were described in a previous paper.[19]

The equilibrium concentrations of ammonium and nitrate ions based on the determination of the total ammonia were calculated according to eqs 5 and 6.

$$[NH_4^+] = 1/2([NH_3]_{tot} - [Na^+] + [V(V)]) \tag{5}$$

$$[NO_3^-] = 1/2([NH_3]_{tot} + [Na^+] - [V(V)]) \tag{6}$$

where $[V(V)]$ is the concentration of vanadate(V) ions and $[NH_3]_{tot}$ is the sum of concentrations of ammonium and nitrate ions.

The distillation method and the flame photometry were used only for solutions with the high concentration of vanadate(V) ions, which interfered with the determination of the concentration of sodium ions with the gravimetric method and ammonium ions with the formalin method.

The composition of the solid phase remaining in equilibrium with the respective solution was determined with the X-ray diffraction method. Solid samples were prepared by filtering off the crystals with the G3 sintered glass crucible under the reduced pressure. Samples were dried in air and subsequently in the desiccator. After reaching the constant mass, the crystals were crushed in the agate mortar and analyzed. The obtained diffractograms were compared with those for standards.[20]

RESULTS AND DISCUSSION

The experimental data on the mutual solubility of salts in the $NH_4NO_3 + NaVO_3 + NH_4VO_3 + NaNO_3 + H_2O$ system at (313 and 323) K are presented in Tables 1 and 2. The data for each experimental point contain the solution density and pH, as well as a concentration of sodium, ammonium, nitrate, and vanadate(V) ions. Also, the mole fractions of sodium and vanadate(V) ions are given, as calculated according to eqs 7 and 8.

$$x_{Na^+} = \frac{[Na^+]}{[Na^+] + [NH_4^+]} \tag{7}$$

$$x_{V(V)} = \frac{[V(V)]}{[V(V)] + [NO_3^-]} \tag{8}$$

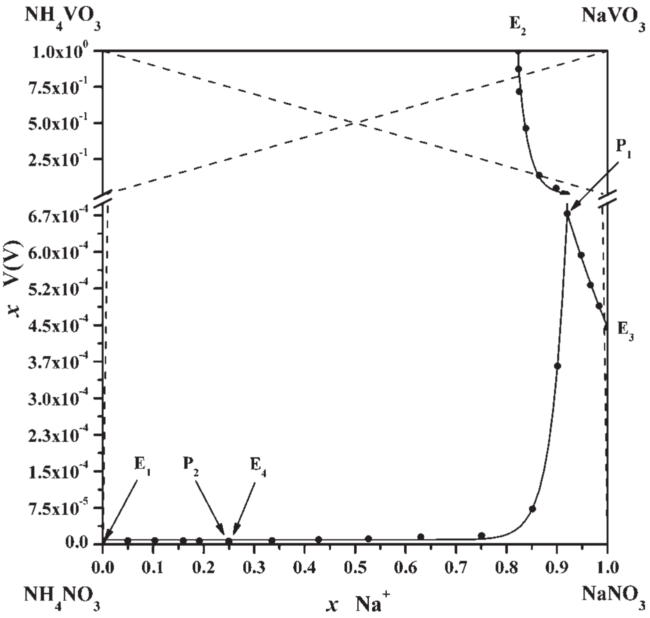

Figure 1. Solubility isotherm for the $NH_4NO_3 + NaVO_3 + NH_4VO_3 + NaNO_3 + H_2O$ system at 313 K. The broken lines indicate the diagonals of the plot.

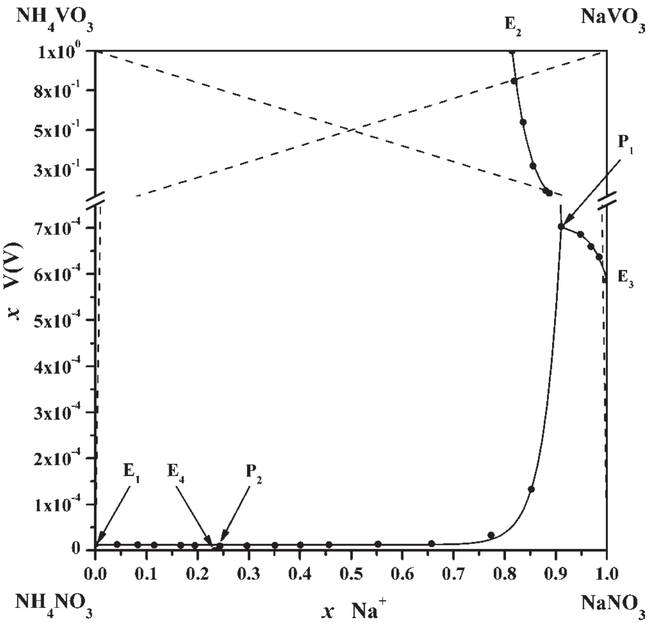

Figure 2. Solubility isotherm for the $NH_4NO_3 + NaVO_3 + NH_4VO_3 + NaNO_3 + H_2O$ system at 323 K. The broken lines indicate the diagonals of the plot.

The comparison of experimental data on water solubility of sodium metavanadate in binary system with the data obtained by other authors (Table 3) indicates a good agreement with the Trypuć and Kiełkowska results.[13] On the other hand, values determined by McAdam and Pierle[22] are significantly different.

The obtained values of the mole fractions of sodium and vanadate(V) ions were used to plot the solubility isotherms for the quaternary system in the planar projection according to

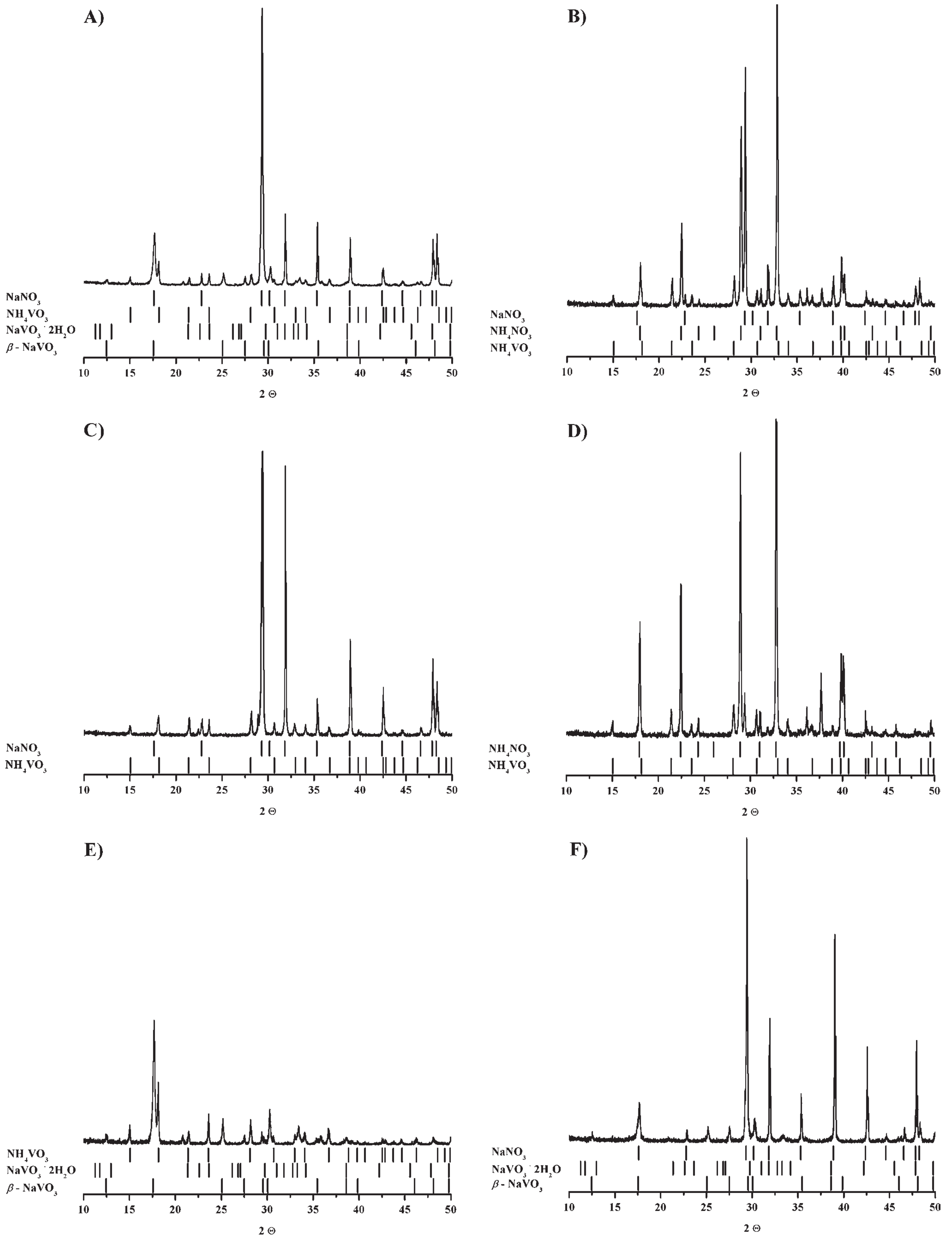

Figure 3. X-ray diffractograms of the solid phase remaining in equilibrium with solutions at 313 K. A, solid phase at point P_1; B, solid phase at point P_2; C, solid phase for fragment P_1-P_2; D, solid phase for fragment E_1-P_2; E, solid phase for fragment E_2-P_1; F, solid phase for fragment E_3-P_1.

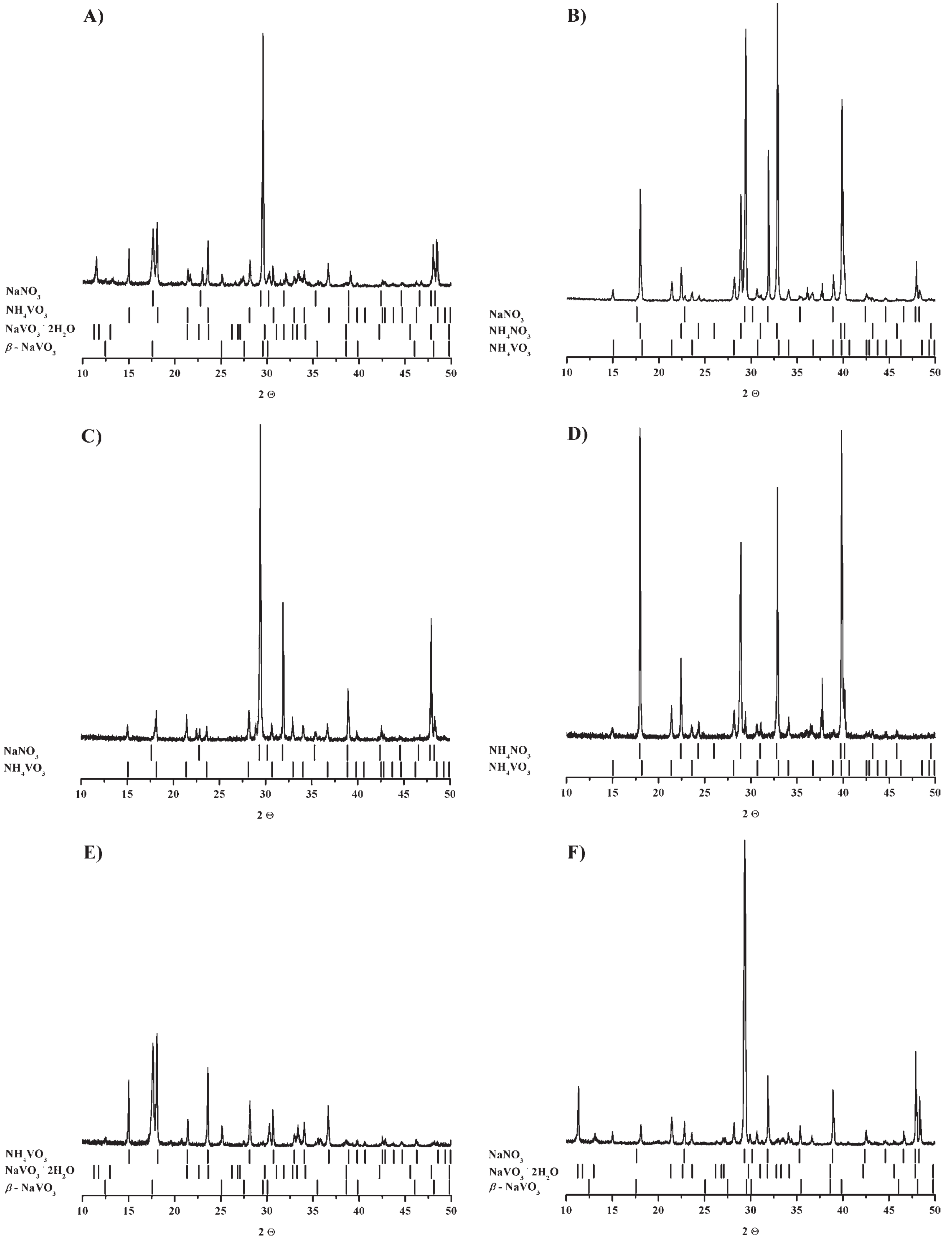

Figure 4. X-ray diffractograms of the solid phase remaining in equilibrium with solutions at 323 K. A, solid phase at point P_1; B, solid phase at point P_2; C, solid phase for fragment P_1—P_2; D, solid phase for fragment E_1—P_2; E, solid phase for fragment E_2—P_1; F, solid phase for fragment E_3—P_1.

Jänecke. The equilibrium plots for the quaternary system at (313 and 323) K are presented on Figures 1 and 2.

The equilibrium plot for the quaternary system results from the projection of the solubility isotherm of that system and its binary and ternary subsystems on the plane defined by the area of a square. The corners of that square represent pure salts NH_4VO_3, NH_4NO_3, $NaVO_3$, and $NaNO_3$. The solubility isotherms of four ternary subsystems containing the common ion and their eutonic points (E_1-E_4) are projected on the edges of the square.

The area of the plots on Figures 1 and 2 contains the solubility isotherms for the quaternary $NaVO_3 + NH_4NO_3 + NH_4VO_3 + NaNO_3 + H_2O$ system. The plots contain the eutonic points P_1 and P_2 for the quaternary system representing the solutions saturated with three salts: P_1, solution saturated with $NaVO_3$, NH_4VO_3, and $NaNO_3$; P_2, solution saturated with NH_4NO_3, NH_4VO_3, and $NaNO_3$. The eutonic solutions for the ternary and quaternary systems (points E_1-E_4, P_1, and P_2) define five fragments of the solubility isotherms. The E_1-P_2 fragment corresponds to the solutions saturated with respect to the solid phase containing ammonium nitrate and metavanadate. The E_4-P_2 section corresponds to the solutions saturated with sodium and ammonium nitrates. The P_1-P_2 represents the solutions saturated with sodium nitrate and ammonium metavanadates. The E_2-P_1 section corresponds to the solutions saturated with sodium and ammonium metavanadates. The E_3-P_1 curve represents the solutions saturated with sodium nitrate and metavanadate. The above curves divide the area of the plot into four parts corresponding to the areas of crystallization of specific components of the system. The area of the crystallization increases in the raw $NH_4NO_3 < NaNO_3 \ll NaVO_3 \ll NH_4VO_3$. It has to be noticed that the area of crystallization of ammonium metavanadate is larger than those for all other components, which indicates that ammonium metavanadate has the lowest solubility in the investigated system. Figures 1 and 2 reveal that the areas of crystallization of $NaNO_3$ and NH_4VO_3 are located next to each other, which indicates that in the investigated system sodium nitrate and ammonium metavanadate constitute the chemically stable pair of salts. These salts can form the mutually saturated solutions. However, the chemically unstable pair of salts in the system are ammonium nitrate and sodium metavanadate. Figures 1 and 2 show that the areas of their crystallization are separated from each other, which proves that they cannot form the mutually saturated solutions.

Data in Tables 1 and 2 indicate that the addition of ammonium metavanadate into the solution E_3, which is saturated with sodium nitrate and sodium metavanadate, results in a reaction opposite to the reaction of conversion of ammonium nitrate into ammonium metavanadate. That phenomenon occurs until the solution is saturated with ammonium metavanadate, that is, until it reaches the composition corresponding to P_1. In the P_1 solution, the minimum of the mole fraction of ammonium ions is observed for solutions saturated with ammonium metavanadate. For that reason the maximum yield of conversion is reached at the P_1 eutonic solution for the quaternary system of the pairs of the exchange salts. The yield of precipitation of sodium metavanadate is determined graphically based on the equilibrium plots (Figures 1 and 2). The straight line is plotted between the corner corresponding to sodium metavanadate and the P_1 point. This line intersects the axis on which the mole fractions of sodium ions are marked. The mole fraction of sodium ions at the intersection of the plotted line with the axis, multiplied by 100 %, gives the maximal yield of the reaction of double exchange. The yields of the conversion determined in that way at (313 and 323) K are (91.8 and 91.0) %, respectively.

The quality composition of the solid phase remaining in equilibrium with solutions, as well as the possibility of formation of the new solid phases in the investigated system, was determined with X-ray diffraction analysis. For solutions saturated with sodium metavanadate (Figures 1 and 2, branches $E_2-P_1-E_3$) it was found that the solid phase is formed mainly by β-$NaVO_3$ and small amounts of $NaVO_3 \cdot 2H_2O$. The obtained results are analogous to those for the ternary systems containing sodium metavanadate ($NaNO_3 + NaVO_3 + H_2O$[11] and $NH_4VO_3 + NaVO_3 + H_2O$[13]). It has been observed that the hydrated form of $NaVO_3$ is unstable and undergoes an allotropic change to form β-$NaVO_3$, even at room temperature. This fact seems to be consistent with the data presented in the paper of Kuok et al.[21]- and McAdam and Pierle.[22] It was found for other compounds (ammonium metavanadate and ammonium and sodium nitrates) that only anhydrous forms are present in solid phase. The typical diffraction patterns for the solid phase samples are presented on Figures 3 and 4.

Tables 1 and 2 contain the pH values of the equilibrated solutions, which for (313 and 323) K are in the ranges 4.16 to 7.69 and 3.90 to 7.26, respectively. For the respective isotherm branches, the increase of pH with the increasing concentration of vanadate(V) ions was observed. For solutions corresponding to $E_1-P_2-P_1$ and E_4-P_2 branches, besides the concentration of vanadate(V) ions, pH values are affected by changes of the concentration of ammonium ions. In solutions corresponding to E_2-P_1 and P_1-E_3 fragments, the decisive factor affecting pH is the concentration of vanadate(V) ions.

■ CONCLUSIONS

On the basis of the experimental data, the phase diagrams were plotted for the $NaVO_3 + NH_4NO_3 + NaNO_3 + NH_4VO_3 + H_2O$ system at (313 and 323) K (Figures 1 and 2). The position of the eutonic points for the quaternary system on the equilibrium plots (Figures 1 and 2) proves that solid phases in points P_1 are incongruently soluble while solid phases in eutonic points P_2 are congruently soluble. The obtained results indicate that in the investigated system the chemically stable pair of salts is sodium nitrate and ammonium metavanadate, while the chemically unstable pair is sodium metavanadate and ammonium nitrate.

Ammonium metavanadate is the salt of the lowest solubility in the investigated system. The area of crystallization of this salt on Figures 1 and 2 is larger than the area for other system components. The low solubility of ammonium metavanadate at P_1 implies the high yield of precipitation of this salt from the postfiltration lye from the SCS method. The determined maximum yields of the conversion (eq 2) at (313 and 323) K are (91.8 and 91.0) %, respectively.

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