

Articles

Solubility Investigations in the NaCl + V₂O₅ + H₂O System from 293 K to 323 K

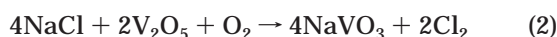
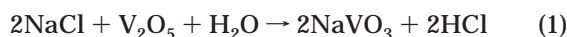
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The mutual solubility of NaCl and V₂O₅ in water in the temperature range 293–323 K is reported. The results are used to plot part of the polythermal solubility surface for the system NaCl + V₂O₅ + H₂O. The data are useful in the determination of the optimum operating parameters for production of sodium metavanadate by reacting NaCl and V₂O₅ in the presence of either steam or oxygen.

Introduction

Sodium carbonate is generated from NaVO₃, which is synthesized from NaCl and V₂O₅ in the presence of steam or oxygen according to the following equations:



The reaction can be carried out without causing serious environmental concerns.^{1–3}

The sodium metavanadate is an intermediate reactant which is subsequently transformed by several unit processes into the final product sodium carbonate (similar to the case of the Solvay method).^{4,5}

Undertaken investigations on the NaVO₃ synthesis, expressed by reactions 1 and 2, indicate clearly that the conversion degree of V₂O₅ into NaVO₃ is strictly correlated with temperature, time of processing, amount of NaCl, steam, or oxygen present in the reaction mixture, and granulation degree of the reagents, that is, V₂O₅ and NaCl.^{1,2,6}

The maximum possible degree of V₂O₅ conversion of about 95% is achieved in a constructed flow reactor at *T* = 823 K, with a 4 h time of processing with 20% NaCl excess and 10 times steam excess. According to literature data, the V₂O₅ conversion degree is estimated at 90% (*T* = 823 K, 10% NaCl excess in the reaction mixture).¹

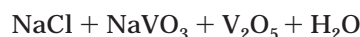
The maximum reaction yield of 66.54 for reaction 2 was achieved with an 8 h duration with reagent amounts maintained at their stoichiometric ratios. Further investigations on optimization of the operating parameters will be carried out.⁷

To determine the optimum operating conditions for the NaVO₃ separation procedure out of the postreaction mixture, a detailed knowledge of the mutual solubility of NaCl, V₂O₅, and NaVO₃ in water is essential. Data for the

Table 1. Comparison of Solubility Data Presented in This Work with the Literature Data for the Binary System NaCl + H₂O

ref	<i>m</i> /(mol·kg ^{−1} of H ₂ O)			
	293 K	303 K	313 K	323 K
this work	6.147	6.195	6.251	6.294
Cohen-Adad and Lorimer ⁸	6.140	6.174	6.223	6.277
Sytniewski ^{9,10}	6.140	6.178	6.224	6.279

following systems have been studied:



This paper deals with the mutual solubility of components, which enables the determination of the series of isothermal sections of the phase diagram for the system NaCl + V₂O₅ + H₂O in the temperature range 293–323 K.

No solubility data have been found in the profound literature review concerning the title system.

A compilation of the solubility data for the binary system NaCl + H₂O has been done recently, and modeling of liquid curves has been performed.^{8–10}

Experimental Part

Chemicals. Analytical purity grade chemicals were used for all of the experiments: NaCl (99.9% POCH S.A. Poland), V₂O₅ (98%, Aldrich Chemical Co., Inc.).

Experimental Procedure. The mutual solubility investigations in the NaCl + V₂O₅ + H₂O system were carried out at 293, 303, 313, and 323 K, employing the isothermal solution saturation technique.

Erlenmeyer flasks, each of 100 cm³ capacity, containing the projected amount of components and water were placed in a thermostated bath until the equilibrium between the solid phase and solution was achieved. All samples were continuously stirred using magnetic stirrers. A Polystat

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Table 2. Experimental Results for the Mutual Solubility of Sodium Chloride and Vanadium (V) Oxide in Water

$\rho/(\text{g}\cdot\text{cm}^{-3})$	$c/(\text{mol}\cdot\text{dm}^{-3})$ NaCl	$10^4 c/(\text{mol}\cdot\text{dm}^{-3})$ V_2O_5	solid phase	$\rho/(\text{g}\cdot\text{cm}^{-3})$	$c/(\text{mol}\cdot\text{dm}^{-3})$ NaCl	$10^4 c/(\text{mol}\cdot\text{dm}^{-3})$ V_2O_5	solid phase
$T = 293 \text{ K}$				$T = 303 \text{ K}$			
1.197	5.413	0	NaCl	1.193	5.426	0.000	NaCl
1.197	5.441	1.071	NaCl	1.194	5.438	0.456	NaCl
1.198	5.451	1.769	NaCl	1.194	5.448	1.082	NaCl
1.198	5.458	2.630	NaCl	1.195	5.457	2.016	NaCl
1.198	5.458	3.110	NaCl	1.195	5.464	3.210	NaCl
1.199	5.459	3.400	NaCl	1.195	5.464	3.981	NaCl
1.199	5.459	4.092	NaCl	1.195	5.463	4.807	NaCl
1.199	5.458	4.913	NaCl	1.196	5.463	5.280	NaCl
1.199	5.458	5.863	NaCl	1.196	5.463	5.939	NaCl, V_2O_5
1.199	5.458	6.385	NaCl, V_2O_5	1.189	4.818	5.940	V_2O_5
1.176	4.792	6.598	V_2O_5	1.161	3.940	6.350	V_2O_5
1.150	4.206	6.920	V_2O_5	1.124	3.305	6.840	V_2O_5
1.127	3.180	7.930	V_2O_5	1.090	2.467	8.021	V_2O_5
1.096	2.081	9.680	V_2O_5	1.066	1.910	9.000	V_2O_5
1.058	1.250	11.67	V_2O_5	1.035	1.320	10.41	V_2O_5
1.027	0.782	13.51	V_2O_5	1.007	0.400	14.53	V_2O_5
1.015	0.310	15.19	V_2O_5	0.999	0.930	18.42	V_2O_5
0.997	0	20.46	V_2O_5	0.998	0	21.60	V_2O_5
$T = 313 \text{ K}$				$T = 323 \text{ K}$			
1.188	5.439	0	NaCl	1.184	5.448	0	NaCl
1.190	5.440	0.074	NaCl	1.186	5.454	0.310	NaCl
1.191	5.445	0.229	NaCl	1.187	5.461	0.620	NaCl
1.192	5.453	0.690	NaCl	1.188	5.465	1.020	NaCl
1.192	5.459	1.121	NaCl	1.188	5.469	1.420	NaCl
1.192	5.463	1.650	NaCl	1.189	5.470	1.698	NaCl
1.192	5.466	1.834	NaCl	1.190	5.474	2.560	NaCl
1.193	5.468	2.650	NaCl	1.190	5.476	3.070	NaCl
1.193	5.469	3.836	NaCl	1.190	5.477	3.699	NaCl
1.193	5.468	4.900	NaCl	1.190	5.475	4.401	NaCl
1.193	5.468	4.493	NaCl	1.191	5.476	4.992	NaCl
1.193	5.467	5.605	NaCl, V_2O_5	1.191	5.475	5.191	NaCl, V_2O_5
1.155	5.030	5.670	V_2O_5	1.172	4.811	5.200	V_2O_5
1.154	4.283	5.820	V_2O_5	1.155	4.091	5.270	V_2O_5
1.110	3.034	6.151	V_2O_5	1.108	3.156	5.650	V_2O_5
1.075	2.390	7.310	V_2O_5	1.061	2.220	7.091	V_2O_5
1.040	1.691	8.751	V_2O_5	1.038	1.403	8.880	V_2O_5
1.021	0.800	11.42	V_2O_5	1.024	0.806	10.95	V_2O_5
1.012	0.319	15.10	V_2O_5	1.001	0.335	13.51	V_2O_5
1.000	0.176	18.43	V_2O_5	1.000	0.124	17.00	V_2O_5
0.999	0	21.85	V_2O_5	0.999	0	22.20	V_2O_5

CC1 thermorelay (Germany), with a precision of $\pm 0.02 \text{ K}$ was used for the experimental equilibrium.

The experimental time of thermostating was 120 h.

After a fixed time interval, stirring was discontinued and solids were sedimented.

The clear equilibrium solution was transferred into a Ostwald pycnometer calibrated at a given temperature. The total pycnometer content was employed for the solution density determination.

The uncertainty of density measurements was estimated to be $\pm 0.002 \text{ g}\cdot\text{cm}^{-3}$.

Then the solution was transferred quantitatively to the graduated flask and diluted using distilled water, and the chloride ion and vanadium concentration measurements were performed.

Analytical Methods. The chloride ion concentration was evaluated using the potentiometric titration method (716 DMS Titrimetric titrator, Switzerland) with a combined silver electrode.^{11–13}

A diluted solution of H_2SO_4 acid (1:9) was introduced into each sample; next each sample was titrated using a 0.1 M solution of AgNO_3 .

Obviously, the presence of vanadium(V) implies a very low repeatability of the end point of titration for low concentrations of Cl^- ions. Therefore, vanadium(V) was reduced using the solution of sodium sulfite in diluted (1:7) sulfuric acid.¹² In all reduced samples, the concentration of chloride ions was evaluated by means of the argentometric method analogous to that employed in solutions without preliminary reduction. The average relative error of the measurements was estimated to be $\pm 0.5\%$.

The concentration of vanadium(V) was determined using the spectrophotometric method with a double beam UV/VIS U-2000 (HITACHI) spectrophotometer. The formation effect of colored complexes by vanadium ions with 4-(2-pyridyloazo)resorcinol (PAR)^{12,14} was employed. This agent is known for its reactivity with vanadium compounds. The optimum pH for the complex stability is determined to be within 5–6 with the maximum absorbency at $\lambda = 543 \text{ nm}$. The sodium salt of PAR was used because of its fair solubility in water. The determination accuracy was $\pm 2\%$.

Identification of Solid Phases. Identification of the solid phases was carried out by an X-ray method using the X-ray diffractometer HZG-4/A-2 (GDR) with continuous registration. The qualitative analysis was based on the distribution curves of the dispersed radiation intensity expressed as $I = f(\theta)$. All diffractograms were inspected for the series of interplanar distance, d , and the relative intensities, I , and compared with the numeric data listed in "The powder diffraction file" and "Rentgenostrukturalne metody identyfikacji minerałów i skał".^{15,16}

Results and Conclusion

The comparison of literature data with the present work for the binary system $\text{NaCl} + \text{H}_2\text{O}$ in the temperature range 293–323 K is presented in Table 1.

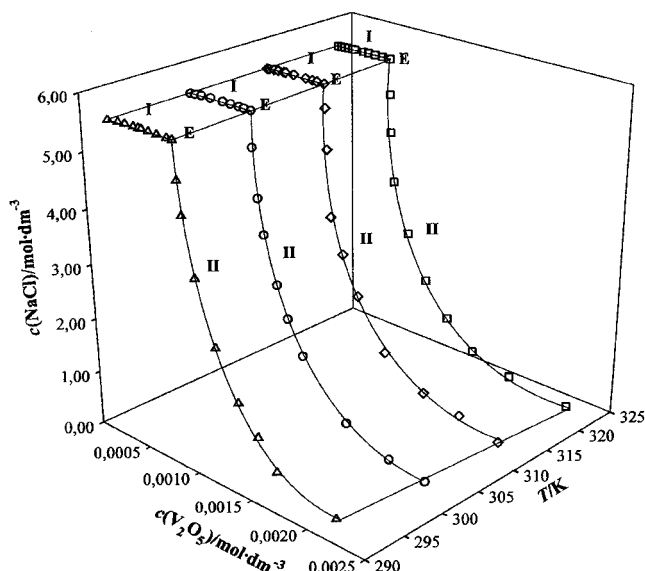


Figure 1. Solubility of NaCl and V_2O_5 in the system $NaCl + V_2O_5 + H_2O$: Δ , 293 K; \circ , 303 K; \diamond , 313 K; \square , 323 K.

Data derived from the quantitative chemical analysis of the equilibrium solutions are included in Table 2.

The collected data gave grounds for the construction of a part of the polythermal solubility surface for the $NaCl + V_2O_5 + H_2O$ system (Figure 1).

Each respective isotherm is composed of two branches. Branch I (Figure 1) of each isotherm describes the sodium chloride concentration changes with increasing concentration of V_2O_5 in equilibrium solution. Branches II of the isotherms represent the concentration changes of V_2O_5 with increasing concentration of NaCl in solution and correspond to the saturated solution of V_2O_5 .

Figure 1 consists of the field of unsaturated solutions extending from the origin to the solubility surfaces, surface I representing saturated solutions with solid-phase NaCl, and surface II representing saturated solutions with solid-phase V_2O_5 . There is also a eutonic line representing doubly-saturated solutions with NaCl and V_2O_5 as the equilibrium solid phases.

The increase in vanadium concentration values toward the eutonic points E implies a very insignificant influence on the sodium chloride solubility in equilibrium solution. The detected difference in the NaCl solubility values in aqueous solution and in the eutonic points is measured to be $-0.045 \text{ mol}\cdot\text{dm}^{-3}$ at $T = 293 \text{ K}$; $-0.037 \text{ mol}\cdot\text{dm}^{-3}$ at 303 K; $-0.028 \text{ mol}\cdot\text{dm}^{-3}$ at 313 K; and $-0.027 \text{ mol}\cdot\text{dm}^{-3}$ at 323 K, respectively. This increment in the NaCl solubility is linked with the vanadium presence in solution and is decreased with the temperature rise.

On the basis of plotted curves (Figure 1) and data analysis (Table 2), it was concluded that the solubility values of NaCl and V_2O_5 change only insignificantly with the temperature rise.

Analysis of the data collected in Table 2 revealed that, in the case of each studied temperature, the densities of saturated equilibrium solutions of NaCl are practically constant with the increase in vanadium concentration

Table 3. Interplanar Distance, d , and the Relative Intensities, I , for V_2O_5 (Radiation Cu $K\alpha$, $\lambda = 0.15418 \text{ nm}$)

exp data		lit. data		exp data		lit. data	
$d/(\text{nm})$	I	$d/(\text{nm})$	I	$d/(\text{nm})$	I	$d/(\text{nm})$	I
0.573	35	0.570	33	0.192	15	0.192	13
0.436	100	0.438	100	0.186	10	0.186	7
0.340	86	0.339	83	0.178	11	0.177	10
0.287	51	0.287	53	0.165	9	0.165	7
0.276	17	0.276	13	0.157	8	0.156	7
0.268	10	0.268	7	0.151	8	0.151	7
0.261	18	0.261	13	0.149	8	0.149	7
0.218	10	0.218	7	0.145	8	0.145	7
0.199	9	0.199	7	0.131	8	0.131	7

values in solution. When the specific eutonic points E are crossed over, the solution density values are rapidly diminished to reach the values which correspond to the density values of V_2O_5 saturated solutions.

An X-ray analysis of the solid phase confirms that, within the temperature range studied, the equilibrium solid phase along branch I is NaCl, while along branch II it is V_2O_5 . Along the eutonic line, both these solid phases occur.

Table 3 gives the d -spacing for V_2O_5 calculated from the diffraction angles using the Bragg equation.

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