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Solubility in the $NaVO_3 + NH_4VO_3 + H_2O$ System

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The solubility of sodium vanadate and ammonium vanadate in the system $NaVO_3 + NH_4VO_3 + H_2O$ in the temperature range 293 K to 323 K has been studied. A section of the solubility polytherm has been drawn. These results are required to determine the optimum conditions for the process of producing sodium carbonate by the modified Solvay method.

Introduction

There have been studies on the method of simultaneous production of sodium carbonate and hydrochloric acid or chlorine based on NaCl and V_2O_5 as the intermediate reagent in the presence of steam or oxygen (U.S. patent, 1967). To determine the optimum conditions for the kinetics of the carbonization process and crystallization of NH_4VO_3 in the modified process of producing sodium carbonate based on the traditional Solvay method, a detailed knowledge of the equilibrium diagram of the reciprocal salt pairs system $NaVO_3 + NH_4HCO_3 + H_2O$ in the oblique projection, according to Janecki (Wiktorow, 1975), is necessary. After the final estimation of the diagram, the data concerning the $NaVO_3$ solubility in water + NH_3 solutions and their vapor pressure, it would be possible to draw certain conclusions referring to the process operating parameters.

Trypuć and Kiełkowska (1995, 1996) recently reported the results of the equilibrium studies on the ternary systems $NaVO_3 + NaHCO_3 + H_2O$ and $NH_4HCO_3 + NH_4VO_3 + H_2O$, which are represented by both square sides of the diagram in its oblique projection.

This paper is a continuation of the investigations carried out formerly and deals with the system $NaVO_3 + NH_4VO_3 + H_2O$. The former equilibrium investigations (Andrejew, 1959) were performed at two temperature points, 285.5 K and 333 K, and did not involve the specific identification of the solid phase composition by an X-ray method. It was determined only on the basis of the given isotherms presented on the triangular diagram—without any differentiation between the hydrated forms of $NaVO_3$ and β-$NaVO_3$. The authors of this paper are concerned mainly with the temperature range 293 K to 323 K, chosen on the basis of the operating parameters used in the Solvay method of producing sodium carbonate (Niederliński et al., 1978; Trypuć and Kiełkowska, 1996).

Experimental Part

The solubility of the sodium vanadate + ammonium vanadate + water system in the temperature range 293 K to 323 K has been investigated by the method of isothermal solution saturation.

The following analytical purity grade salts were used: $NaVO_3$ (>99% Merck) and NH_4VO_3 (99%, Aldrich Chemical Co. Ltd.).

Erlenmeyer flasks, each 100 cm^3 capacity, containing suitable amounts of salts and distilled water were placed in a thermostat and stirred by means of the magnetic stirrer. It guaranteed the complete stabilization of the equilibrium between the solution and the solid phase at the given temperature. The time of thermostating the particular samples should not be shorter than 96 h, given the fact that the equilibrium state is attained rather slowly. It has also been noted that placing the flasks for several minutes in the ultrasonic bath considerably speeds up the time of reaching an equilibrium condition. The time shortens to 72 h. The temperature was measured using the mercury thermometer with an accuracy of ±0.1 K.

After the set time limit, stirring was discontinued and the clear solution was sampled to the calibrated, at the given temperature, Ostwald pycnometer. The total content of this pycnometer was used to determine the solution densities and specifically the concentration of vanadium, sodium, and ammonium ions after their appropriate dilution.

The density was measured with an accuracy of ±0.002 $g\cdot cm^{-3}$.

The concentration of sodium ions was determined by the Kolthoff and Barbera balance method in the form of sodium zinc uranyl acetate (Furman, 1962). The accuracy of the measurement was less than ±1%.

The concentration of NH_4^+ ions was determined by the distillation method with the addition of Devarda's alloy, which protected NH_3 from oxidation to N_2, under the influence of VO_3^- ions (Struszyński, 1954), with an accuracy less than ±1%.

The concentration of VO_3^- ions was determined using the potentiometric titration with a 0.1 M solution of iron(II) ammonium sulfate hexahydrate (Mohr's salt) in the ligand's buffered solution Zn(II)−EDTA (Umetsu et al., 1991). Potentiometric titration was performed using the automatic titrator 716 DMS TITRINO, with a combination platinum electrode supplied by Methrom Switzerland. Considering the maximum buffer capacity, 1.0×10^{-2} $mol\cdot dm^{-3}$ of EDTA and 2.0×10^{-2} $mol\cdot dm^{-3}$ Zn(II) (zinc sulfate heptahydrate) were used (Tanaka, 1963; Tanaka and Nakagawa, 1965). The titration of vanadium(V) with iron(II) in the presence of EDTA was performed in the dark, since vanadium(V) is slowly reduced by the excess of EDTA, even in the absence of iron(II) and the reduction is accelerated by light (Tanaka and Ishida, 1966). The accuracy of the measurement was less than ±1%.

The identification of the solid phases in the state of equilibrium with the solution was carried out by both chemical and X-ray methods. The qualitative analysis of the precipitate was performed using an X-ray diffractometer HZG-4/A-2 (GDR) with continuous registration. The X-ray analyses of the solid phases were based on the distribution curves of the dispersed radiation intensity $I = f(\theta)$.

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Table 1. Solubility in the System $NaVO_3$ + NH_4VO_3 + H_2O

	ρ/	c/mol·dm^{-3}		
T/K	g·cm^{-3}	$NaVO_3$	NH_4VO_3	composition of the solid phase
293	1.124	1.387	0.000	$NaVO_3·2H_2O$
	1.126	1.379	0.045	$NaVO_3·2H_2O$
	1.128	1.368	0.097	$NaVO_3·2H_2O$
	1.129	1.363	0.124	$NaVO_3·2H_2O$
	1.132	1.355	0.158	$NaVO_3·2H_2O$
	1.136	1.352	0.211	$NaVO_3·2H_2O$
	1.138	1.351	0.246	$NaVO_3·2H_2O$
	1.138	1.350	0.265	$NaVO_3·2H_2O$, NH_4VO_3
	1.123	1.167	0.239	NH_4VO_3
	1.096	0.911	0.197	NH_4VO_3
	1.074	0.680	0.163	NH_4VO_3
	1.056	0.513	0.138	NH_4VO_3
	1.027	0.231	0.090	NH_4VO_3
	1.012	0.088	0.065	NH_4VO_3
	1.001	0.000	0.050	NH_4VO_3
303	1.138	1.610	0.000	$NaVO_3·2H_2O$, β-$NaVO_3$
	1.141	1.611	0.041	$NaVO_3·2H_2O$, β-$NaVO_3$
	1.152	1.611	0.158	$NaVO_3·2H_2O$, β-$NaVO_3$
	1.156	1.613	0.208	$NaVO_3·2H_2O$, β-$NaVO_3$
	1.158	1.614	0.231	$NaVO_3·2H_2O$, β-$NaVO_3$
	1.162	1.616	0.263	$NaVO_3·2H_2O$, β-$NaVO_3$
	1.164	1.618	0.285	$NaVO_3·2H_2O$, β-$NaVO_3$
	1.170	1.620	0.352	$NaVO_3·2H_2O$, β-$NaVO_3$, NH_4VO_3
	1.156	1.459	0.324	NH_4VO_3
	1.138	1.299	0.297	NH_4VO_3
	1.105	0.979	0.241	NH_4VO_3
	1.069	0.685	0.196	NH_4VO_3
	1.024	0.236	0.118	NH_4VO_3
	1.006	0.075	0.086	NH_4VO_3
	1.002	0.000	0.074	NH_4VO_3
313	1.115	1.823	0.000	$NaVO_3·2H_2O$, β-$NaVO_3$
	1.158	1.865	0.047	$NaVO_3·2H_2O$, β-$NaVO_3$
	1.166	1.912	0.094	$NaVO_3·2H_2O$, β-$NaVO_3$
	1.175	1.943	0.158	$NaVO_3·2H_2O$, β-$NaVO_3$
	1.189	2.015	0.245	$NaVO_3·2H_2O$, β-$NaVO_3$
	1.203	2.078	0.347	$NaVO_3·2H_2O$, β-$NaVO_3$
	1.207	2.085	0.376	$NaVO_3·2H_2O$, β-$NaVO_3$
	1.220	2.115	0.455	$NaVO_3·2H_2O$, β-$NaVO_3$, NH_4VO_3
	1.209	2.006	0.435	NH_4VO_3
	1.176	1.672	0.382	NH_4VO_3
	1.139	1.297	0.323	NH_4VO_3
	1.067	0.681	0.216	NH_4VO_3
	1.029	0.287	0.154	NH_4VO_3
	1.012	0.131	0.130	NH_4VO_3
	1.002	0.000	0.105	NH_4VO_3
323	1.179	2.092	0.000	$NaVO_3·2H_2O$, β-$NaVO_3$
	1.197	2.195	0.107	$NaVO_3·2H_2O$, β-$NaVO_3$
	1.210	2.261	0.184	$NaVO_3·2H_2O$, β-$NaVO_3$
	1.218	2.302	0.245	$NaVO_3·2H_2O$, β-$NaVO_3$
	1.237	2.346	0.366	$NaVO_3·2H_2O$, β-$NaVO_3$
	1.253	2.372	0.487	$NaVO_3·2H_2O$, β-$NaVO_3$
	1.256	2.381	0.504	$NaVO_3·2H_2O$, β-$NaVO_3$
	1.262	2.385	0.543	$NaVO_3·2H_2O$, β-$NaVO_3$, NH_4VO_3
	1.233	2.112	0.497	NH_4VO_3
	1.198	1.818	0.448	NH_4VO_3
	1.148	1.382	0.377	NH_4VO_3
	1.097	0.889	0.296	NH_4VO_3
	1.059	0.523	0.237	NH_4VO_3
	1.029	0.255	0.193	NH_4VO_3
	1.003	0.000	0.147	NH_4VO_3

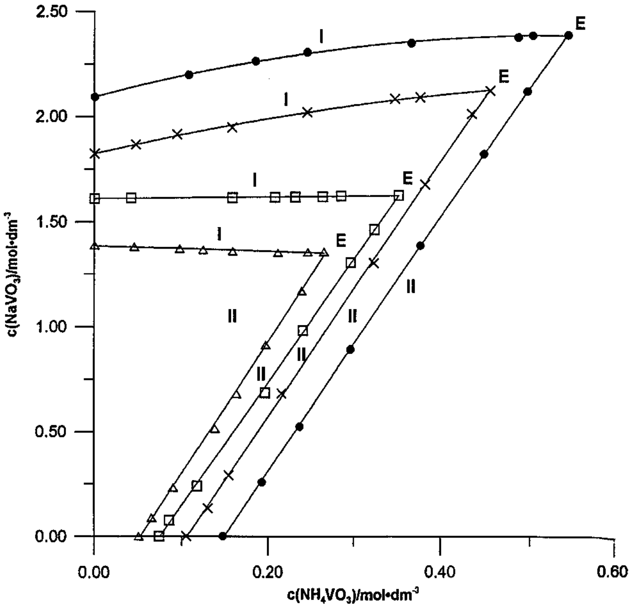

Figure 1. Solubility of $NaVO_3$ and NH_4VO_3 in the $NaVO_3$ + NH_4VO_3 + H_2O system: (△) T = 293 K; (□) T = 303 K; (×) T = 313 K; (●) T = 323 K. Branches I correspond to the saturated solutions of $NaVO_3$ with the NH_4VO_3 concentration increasing toward the eutonic points. Branches II correspond to the saturated solutions of NH_4VO_3 with the $NaVO_3$ concentration increasing toward the eutonic points. The eutonic points E correspond to the saturated solutions toward $NaVO_3$ and NH_4VO_3 salts.

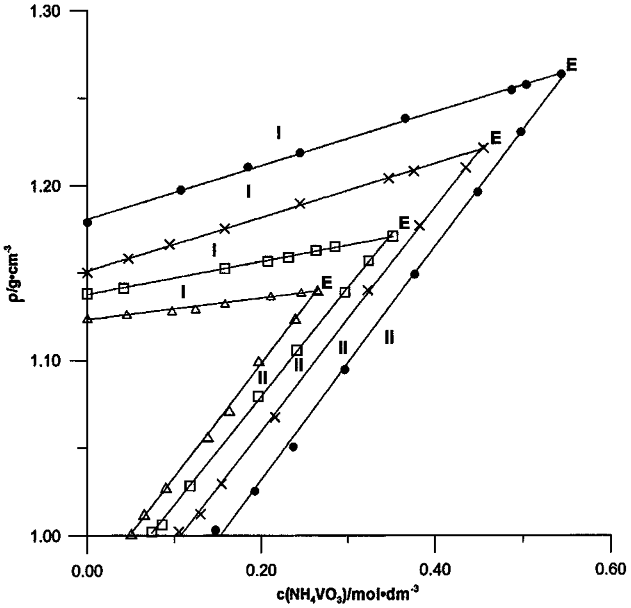

Figure 2. Density–concentration relationships of NH_4VO_3 in the $NaVO_3$ + NH_4VO_3 + H_2O system: (△) T = 293 K; (□) T = 303 K; (×) T = 313 K; (●) T = 323 K.

Results and Discussion

The obtained results concerning the solubility of the sodium vanadate + ammonium vanadate + water system are presented in Table 1. On the basis of these results a section of the polytherm of the $NaVO_3$ + NH_4VO_3 + H_2O system (Figure 1) and the dependence of the solution density on the concentration of NH_4VO_3 (Figure 2) have been constructed.

The specific course of the solubility isotherms (Figure 1) indicate that, for both temperatures 313 K and 323 K with an increase of NH_4VO_3 concentration, in the saturated solutions toward $NaVO_3$, the concentration of $NaVO_3$ increases in a nonlinear mode toward the eutonic points (branch I). A nonlinear increase of the $NaVO_3$ solubility appears to be caused by the changes in the solid phase composition, e.g. the percent rise of an allotropic form of $NaVO_3$. For the specific temperature point of 303 K, the $NaVO_3$ concentration practically does not depend on the concentration of NH_4VO_3. The difference between the $NaVO_3$ solubility in the eutonic point and that with $c(NH_4VO_3) = 0$ is 0.01 mol·dm^{-3}. It points to the solubility increase as compared to the pure salt of 0.62%. However, for the temperature 293 K, the concentration of $NaVO_3$ inconsiderably decreases toward the eutonic point.

The analysis of the course of branches II for each of the particular isotherms proves that the $NaVO_3$ concentration influence on the solubility of NH_4VO_3 is considerable and shows a linear dependence. The rise in the concentration (δ_c/mol·dm^{-3}) of NH_4VO_3 for the corresponding isotherms (i.e. the difference between the concentration of NH_4VO_3 in the eutonic point and that in the saturated solution) amounts to, at $T = 293$ K, $\delta_c = 0.215$; at 303 K, $\delta_c = 0.278$; at 313 K, $\delta_c = 0.350$; and at 323 K, $\delta_c = 0.396$. As far as the operating conditions of the carbonization process of $NaVO_3$ ammonia brine are concerned, the salting-out effect seems to be quite profitable. It enables running the process with a slight amount of $NaVO_3$ in the solid phase.

The solubility of $NaVO_3$ and NH_4VO_3 increases with an increase in temperature. The concentration of $NaVO_3$ at $T = 323$ K is about 51% higher than that at $T = 293$ K, whereas the concentration of NH_4VO_3 is 194% higher. The solubility of NH_4VO_3 is far more dependent on temperature than the solubility of $NaVO_3$.

On the basis of the observed density changes of the solutions, it can be concluded that with the increase in the NH_4VO_3 concentration (for the saturated $NaVO_3$ solutions) the densities of the solutions also increase and reach their maximum at the eutonic points E. After crossing these points, the densities diminish gradually, reaching the values corresponding to the densities of the saturated solutions of NH_4VO_3 (Figure 2).

The existence of only one eutonic point on each of the isotherms and the X-ray analysis of the precipitates proves that in the investigated system a new solid phase is not formed (Sułajmankułov, 1971).

The solid phase composition, determined directly after its sampling on the basis of the X-ray analysis of the precipitates, is presented in Table 1. At $T = 293$ K $NaVO_3$ exists only in the hydrated form, whereas at higher temperatures additionally β-$NaVO_3$ appears. The X-ray analysis of the examined precipitates was also carried out after 24 and 48 h. 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. (1995).

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