Influence of temperature, vanadium concentration, and degree of acidification of solution on composition of solid products. I. Formation of cadmium vanadates in the medium of acetic and perchloric acids

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The influence of vanadium concentration, acidity, and temperature of the solution on composition of the products of the reactions involving binary replacement in the systems $NaVO_3$ — CH_3COOH — $Cd(CH_3COO)_2$ — H_2O and $NaVO_3$ — $HCIO_4$ — $Cd(CH_3COO)_2$ — H_2O has been studied. It has been revealed that $Cd(VO_3)_2 \cdot 4H_2O$ is predominantly formed in both systems at 20°C. Under certain conditions, even $Na_4CdV_{10}O_{28} \cdot 24$ — $26H_2O$ arises in a system containing CH_3COOH . With increasing temperature of the solutions, the equilibrium is shifted towards formation of less condensed vanadate ions, which manifests itself in increasing content of $Cd_2V_2O_7$ in the solid product.

Изучено влияние концентрации ванадия, кислотности и температуры раствора на состав продуктов реакций двойного замещения в системах NaVO₃—CH₃COOH—Cd(CH₃COO)₂—H₂O и NaVO₃—HClO₄—Cd(CH₃-COO)₂—H₂O. Обнаружено, что при 20°C образуется в обеих системах преимущественно Cd(VO₃)₂ · 4H₂O. В системе с CH₃COOH образуется при некоторых условиях также Na₄CdV₁₀O₂₈ · 24—26H₂O. С ростом температуры растворов равновесие смещается в сторону образования менее конденсированных ванадат-ионов, что проявляется в увеличенном содержании Cd₂V₂O₇ в твердом продукте.

The investigation of the dependence of composition of solid vanadates containing some elements on pH of the reaction medium was the topic of several papers published recently [1-8]. The investigation described in these papers was carried out at laboratory temperature or 20°C. It must be stated that the contemporary study of the factors affecting the composition of solid vanadates is not adequately concerned with a so important factor as temperature. The reaction products of binary replacement formed at varying degree of acidity of sodium vanadate solution, different vanadate concentrations, and different temperatures are investigated in this paper.

Experimental

 $NaVO_3$ 2H₂O was prepared according to literature [9]. Other chemicals used were anal. grade reagents of Czechoslovak production.

Concentrations of the solutions of cadmium acetate and sodium vanadate were 0.5, 0.1, and 0.05 N. The degree of acidity Z is given by the ratio of the amount of substance of acid used to the amount of substance of sodium metavanadate. The values of Z varied in the range 0.1-0.7. This range rendered possible the formation of cadmium decavanadate and at higher temperatures even cadmium hexavanadate. The mole ratio Cd V was 3 10. Redistilled water was used for the preparation of solutions.

As complicated reactions take place in solutions of vanadates, the acidified solutions of sodium vanadate were allowed to settle before proper synthesis. The establishment of equilibrium was checked by pH measurement.

cv	Z	20°C			40°C			60°C		
		pНı	pH₂	Product	pНı	pH ₂	Product	рHı	pH ₂	Product
0.5	0.1	6.92	6.93	Α	6.05	5.98	A + C	5.91	5.10	C + A
	0.2	6.71	6.21	Α	6.00	5.87	Α	5.83	5.40	C + A
	0.3	6.44	6.20	Α	6.00	5.65	В	5.55	4.89	C + A
	0.4	6.10	6.00	D	5.99	5.88	Α	5.40	4.59	C+B'+A
	0.5	5.60	5.30	A + C	5.70	5.31	C + B	5.11	4.80	B+C+A
	0.6	5.40	5.40		5.28	5.34	A + C	4.95	4.80	B + A
	0.7	5.20	5.20	_	5.15	5.15	—	4.80	4.60	B+C+A
0.1	0.1	6.69	6.63	Α	6.20	5.68	C + B + A	5.84	5.10	C + A
	0.2	6.30	6.20	Α	6.11	5.70	C + B	5.64	4.91	C + A
	0.3	6.29	5.80	Α	5.95	5.75	A + B + C	5.55	4.91	C + B + A
	0.4	6.09	5.71	A + C	5.47	5.07	B + A	5.27	4.89	B+C+A
	0.5	5.65	5.29	Α	5.18	5.19	Α	5.20	4.90	B+C+A
	0.6	5.30	5.30	<u> </u>	5.11	5.27	B + C	5.10	4.87	B+C+A
	0.7	4.92	4.92	_	5.09	5.09		5.00	4.80	B+C+A
0.05	0.1	6.59	6.12	Α	6.10	5.44	A + C	5.93	4.94	C + A
	0.2	6.42	5.88	Α	6.00	5.32	A + C	5.92	4.74	C + A
	0.3	6.21	5.78	A + C	5.95	5.54	B+C+A	5.81	5.80	C + A
	0.4	5.92	5.67	A + C	5.87	5.21	B+C+A	5.21	5.05	B + C
	0.5	5.51	5.19	A + C	5.40	4.81	B+C	4.98	4.71	B+C
	0.6	5.29	5.29		5.21	5.19	Α	4.90	4.61	В
	0.7	5.09	5.09		5.15	5.15	-	4.75	4.70	В

Table 1

Results of the syntheses in the system NaVO₃-CH₃COOH-Cd(CH₃COO)₂-H₂O

 $pH_1 - pH$ of the solution of sodium vanadate after stabilization; $pH_2 - pH$ of filtrate.

 $A - Cd(VO_3)_2 \cdot 4H_2O; B = \alpha - Cd(VO_3)_2; C = Cd_2V_2O_7; D = Na_4CdV_{10}O_{28} \cdot 24 - 26H_2O.$

The first compound is a predominant component of the mixture.

7	'n	ы	P	2		
	u	$\boldsymbol{\omega}$	c	4		

c _v	z	20°C			40°C			60°C		
		pH1	pH₂	Product	рНı	pH₂	Product	pНı	pH₂	Product
0.5	0.1	6.86	6.65	Α	5.97	5.55	A + C	5.75	4.90	C + A
	0.2	6.70	6.50	Α	5.86	5.56	A + C	5.65	4.70	C + A
	0.3	6.33	6.40	Α	5.73	5.43	B+C	5.61	5.12	C + B + A
	0.4	5.94	5.50	Α	5.40	4.80	B+C	5.40	4.88	C + B + A
	0.5		_	—		-		4.98	4.71	B+C+A
0.1	0.1	6.76	6.47	A	5.98	5.55	A + C + B	5.70	4.80	C + A
	0.2	6.65	6.26	Α	5.87	5.55	A + C + B	5.68	4.71	C + A
	0.3	6.30	5.75	Α	5.85	5.60	B+C+A	5.42	4.91	C + B + A
	0.4	6.06	5.40	Α	5.34	4.70	B+C+A	5.28	4.61	C + B + A
	0.5	5.00	5.10	Α	4.52	5.00	B+C+A	5.11	4.45	B + C + A
0.05	0.1	6.69	6.16	Α	5.80	5.50	A + C	5.50	4.93	C+B+A
	0.2	6.52	6.00	Α	5.79	5.40	A + C + B	5.46	4.86	C + A
	0.3	6.31	5.60	Α	5.54	4.90	B+C+A	5.39	4.96	C + A
	0.4	6.08	5.60	Α	5.40	4.91	B+C	5.35	4.90	C + B + A
	0.5	4.61	5.20	Α	4.42	4.58	A + B + C	4.78	4.52	B+C+A

Results of the syntheses in the system NaVO₃-HClO₄-Cd(CH₃COO)₂-H₂O

During reactions, a constant volume of the reaction solution was maintained. Since it was found in preliminary experiments that the composition of product was also affected by the time of its contact with the solution, the product was isolated at the latest 15 min after its formation. The experiments were carried out at 20, 40, and 60°C. The composition of the products obtained was determined by chemical analysis and confirmed by infrared spectro-10-12 as well as X-ray phase analysis [13, 14]. The results of syntheses are given in Tables 1 and 2.

The content of cadmium in the products obtained was estimated complexometrically using Eriochrom Black T [15] as an indicator. The content of vanadium(V) was determined titrimetrically with FeSO₄ [15]. The presence of vanadium(IV) was checked manganometrically [15]. The content of sodium was estimated by flame photometry [16] using a photometer (Zeiss, Jena), model III. The crystal water was determined gravimetrically by drying up to 350°C as well as by calculation (100 minus percentage of CdO minus percentage of V₂O₅).

The pH value of the solutions was measured on a Radelkis 201/1 pH-meter with a combined glass Ag/AgCl electrode. The infrared spectra (700-1200 cm⁻¹) were taken on a Perkin—Elmer instrument, type 221, by using the nujol technique. The powder diffraction records were obtained on a Philips X-ray diffractometer with a goniometer PW 1058 by using the CuK_a radiation.

Discussion

The investigation of the equilibrium establishment in acidified solutions of sodium vanadate has shown that the time of pH stabilization depends on the acid used. While the pH value got settled practically in 75 min at 20°C in the presence of acetic acid (this time decreased with dilution of the solutions), this time was several times longer in the presence of perchloric acid (the pH value got settled in 12 h in 0.5 N solutions and in 20—24 h in solutions of lower concentration). The increasing temperature of sodium vanadate solutions influenced the rate of pH stabilization differently according to the acid used for acidifying. As for acetic acid, the temperature had no effect on stabilization, but if the solutions were acidified with perchloric acid, the time necessary for pH stabilization was reduced approximately to one quarter at higher temperatures when compared with the value found at 20°C.

It results from chemical analysis, X-ray phase analysis, and infrared spectra of products obtained from the system NaVO₃-CH₃COOHthe solid -Cd(CH₃COO)₂-H₂O that the main product of syntheses at 20°C with all concentrations of vanadium and almost in the whole investigated range of the degree of acidity is $Cd(VO_3)_2 \cdot 4H_2O$ which is sometimes contaminated by the traces of $Cd_2V_2O_7$. An exception is represented by the synthesis in which Z = 0.4and $c_v = 0.5 \text{ mol } l^{-1}$ Under these conditions, the binary decavanadate arises primarily (Table 1). However, metavanadate of the above-mentioned composition is obtained again if this binary decayanadate is separated from the solution. It must be emphasized that this is the only case when decavanadate was obtained as product of the investigated syntheses. If the solution exhibited a higher degree of acidity than the previous one, a mixture of Cd(VO₃)₂ · 4H₂O and Cd₂V₂O₇ was obtained instead of the assumed decavanadate. This fact is surprising, in particular, in confrontation with general information about composition of the vanadates obtained from acid solutions. The formation of cadmium bivanadate is especially interesting because analogous compounds of alkali and alkaline earth metals do not originate in acid but in alkaline solutions. These facts could be so explained that a higher molar concentration of decayanadate ions than the concentration of the saturated solution of the above-mentioned sodium-cadmium decavanadate is present in the solution of sodium vanadate at Z = 0.4. Another addition of acid into solution must produce such conditions which are favourable for the formation of metavanadate and divanadate but not for decavanadate. It seems that a small difference in solubility of Cd(VO₃)₂ · 4H₂O and Cd₂V₂O₇ plays a dominant role in this case. Therefore the composition of the solid products must be considerably affected not only by the complicated equilibrium processes which take place in the solutions of vanadates but also by the concentration of cadmium in the solution. An increase in acidity of the solution over the value 0.5 results only in an increase in solubility of all cadmium vanadates which come into consideration, therefore no solid product was obtained at Z > 0.5.

It is obvious from Tables 1 and 2 that an increasing temperature of the solutions of sodium vanadate is connected with a decreasing of pH value. That might be due to a certain shift in equilibrium in the sense of formation of less condensed vanadate ions in the solution. This is also indicated by the fact that the amount of $Cd_2V_2O_7$ in the products increases with temperature.

At 40°C, $Cd(VO_3)_2 \cdot 4H_2O$ still represents a considerable part of the solid products in which α -Cd(VO₃)₂ is also present besides Cd₂V₂O₇. If the temperature of reaction solutions rises above 60°C, the content of cadmium metavanadate tetrahydrate in the products decreases to such extent that it represents only an admixture. The amount of this admixture depends on the rate with which the product separates from the solution. The major component of the product, at the highest investigated temperature, is Cd₂V₂O₇ (at Z = 0.1-0.3) or α -Cd(VO₃)₂ (at Z > 0.5).

When the solutions of sodium metavanadate were acidified with perchloric acid to higher values of Z, a red-brown precipitate was formed. Therefore it was not possible to investigate in the system $NaVO_3$ — $HClO_4$ — $Cd(CH_3COO)_2$ — H_2O equal range of Z as in preceding case. On the basis of the experimental results obtained with this system, it may be stated that $Cd(VO_3)_2 \cdot 4H_2O$ arises as the only product with all concentrations of vanadium and values of Z at 20°C. It means that the differences in solubility of cadmium divanadate, metavanadate, and decavanadate are greater in the medium of perchloric acid than in the medium of acetic acid. An increasing temperature of the reaction solutions results in the formation of mixtures which are analogous to those already described.

The results obtained with both above systems show that not only the factors already discussed but also the choice of acid is important for the preparation of pure poorly soluble vanadates. In our case, the drawback accompanying the use of perchloric acid (longer time of pH stabilization, smaller range of Z, impossibility of preparing solid decavanadate at constant volume of solution) has been compensated by higher purity of $Cd(VO_3)_2 \cdot 4H_2O$ in comparison with the product obtained in acetate medium.

As for the preparation of particular poorly soluble polyvanadates of a given element, the time of contact of the precipitate with solution is also important.

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