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PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

Reaction of Bismuth Nitrate with Sodium Citrate in Water–Glycerol Solutions

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Abstract—The reaction in a $Bi(NO_3)_3$–Na_3Hcit–(H_2O + glycerol)[1] system was studied in a wide range of component ratios by the solubility method and pH-metry in combination with chemical analysis of solid phases. Poorly soluble phases of $Bi(Hcit)_x(OH)_{3(1-x)} \cdot mH_2O$ ($x < 1$) and sodium bismuth citrate $NaBiCit \cdot 3H_2O$ were obtained. The compounds synthesized were characterized, and their compositions were refined by X-ray diffraction, DTG, and IR spectroscopy.

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Bismuth compounds find wide use, particularly, as pharmaceticals [1]. Therefore, bismuth salts with carboxylic acids are of interest.

In this work, we studied the interactions, composition, and formation conditions of compounds in the $Bi(NO_3)_3$–Na_3Hcit–(H_2O + glycerol) system. It is known that the dissolution of bismuth nitrate in water is accompanied by its hydrolysis to poorly soluble bismuth oxy- and hydroxynitrates [2]. Bismuth nitrate is readily soluble in nitric acid, but at low concentrations of the latter (0.1–0.2 N) these solutions are also rather unstable. Stable in time highly concentrated solutions (up to ~1 g/mL $Bi(NO_3)_3 \cdot 5H_2O$) are formed when mixtures of water with polyhydric alcohols (glycerol, mannitol, and others) are used as solvents. It can be assumed that the bismuth ion with polyatomic alcohol forms associates that are sufficiently stable to retain bismuth in the solution and simultaneously make it possible to completely precipitate bismuth as a poorly soluble compound.

EXPERIMENTAL

Neutral bismuth citrate was used both as a sample synthesized by us and as a commercial high-purity grade reagent. The compounds synthesized in the system were characterized by X-ray diffraction (DRON-3 diffractometer, CuK_α radiation), DTA (Netzsch STA-409), and IR spectroscopy (Carl Zeiss UR-20, KBr pellets).

The starting solutions (0.195 mol/L $Bi(NO_3)_3 \cdot 5H_2O$ and 0.5 mol/L $Na_3Hcit \cdot 5.5H_2O$) were prepared using a mixture of water with glycerol in the volume ratio of 2 : 1. with a constant content of $Bi(NO_3)_3 \cdot 5H_2O$ in each sample (0.0049 mol), the amount of the precipitating agent was gradually increased over a wide interval: the initial molar ratios n = [Cit] : [Bi] ranged from 0.25 to 8.0. The total volume of a sample was 100 mL. The precipitates formed were separated by filtration and washed with an H_2O –glycerol (2 : 1) mixture and then with 50% ethanol. The solid phases washed were dried in air at room temperature until a constant weight was achieved.

For chemical analysis, samples were dissolved in HNO_3. Bismuth was precipitated in the form of $BiPO_4$. To determine the citrate ion, an sample of the substance was burnt in an oxygen flow and examined on a Carlo Erba 1108 analyzer. This method also made it possible to monitor the nitrate ion content in the compound.

The precipitation of sodium zink uranyl acetate, after bismuth was preliminarily separated as BiOCl, and potentiometric titration with the OP-Na-0711-P Na-selective electrode (Radelkis, Hungary) were used for sodium determination.

RESULTS AND DISCUSSION

According to visual observation data (Fig. 1a), the amount of the poorly soluble bismuth compound precipitated (phase I) upon the addition of the precipitating agent increases up to $n \sim 1$; then, beginning with $n \sim 1.2$–1.3, the precipitate gradually goes to the solution again and is dissolved completely at $n \sim 1.5$–1.6. The corresponding noticeable break is observed in the pH curve. The solution formed is metastable (its stability ranges within 10–15 min, depending on the precipitation conditions) and with time again precipitates solid

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[1] Hereafter, according to foreign publications, Hcit = $C_6H_5O_7^{3-}$, and Cit = $C_6H_4O_7^{4-}$.

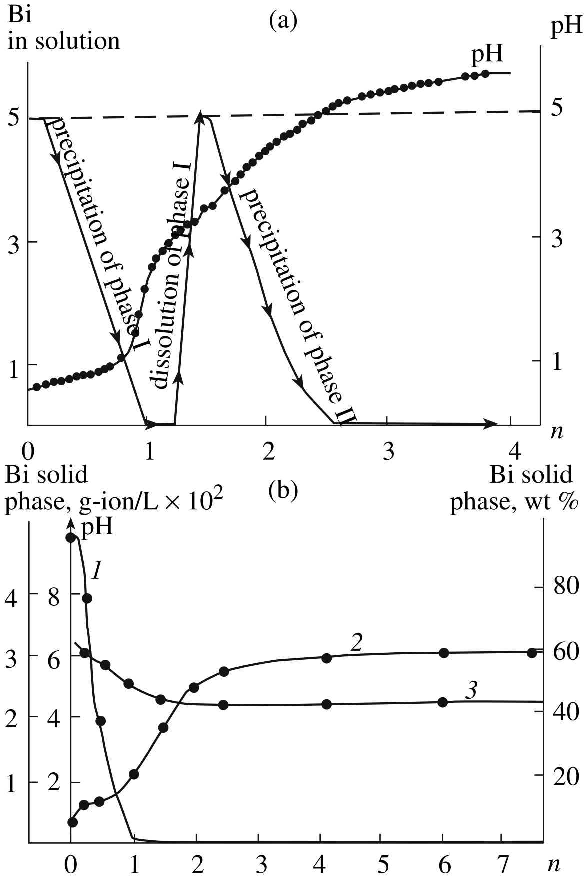

Fig. 1. Interactions in the $Bi(NO_3)_3$–Na_3Hcit–(H_2O + glycerol) system: (a) nonequilibrium and (b) equilibrium conditions.

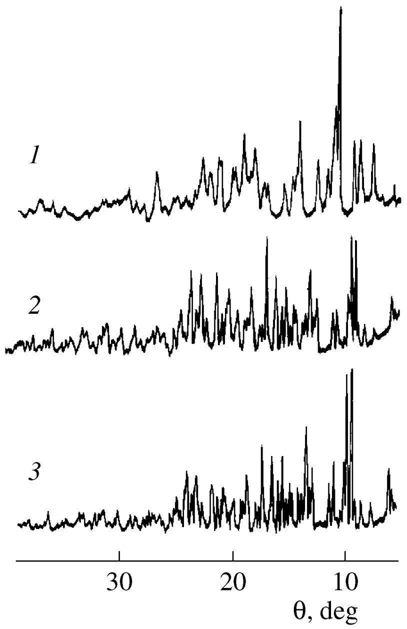

Fig. 2. Diffraction patterns of (*1*) BiHcit (anhydrous) and reaction products of BiHcit (anhydrous) with an aqueous solution of (*2*) Na_3Hcit and (*3*) $NaBiCit \cdot 3H_2O$.

phase II, which is also poorly soluble in mixtures of water with glycerol.

To achieve equilibrium, samples were stirred for 6 h and then stored for 1–2 days. The equilibrium concentrations of bismuth in the liquid phases, the pH values of the equilibrium filtrates, and the compositions of the compounds formed in the $Bi(NO_3)_3$–Na_3Hcit–(H_2O + glycerol) system are given in the table and in Fig. 1b.

The bismuth concentration in the liquid phases (Fig. 1b, curve *1*) decreases with an increase in n, and beginning with $n = 2.0$, bismuth in the filtrates cannot be determined by gravimetry. The pH value of the equilibrium filtrates changes substantially from 0.5 to 5.0 (Fig. 1b, curve *2*) in a range of the initial component ratios $n = 0$–2. In the solid phases, the Bi percentage (Fig. 1b, curve *3*) decreases gradually. In the interval $n = 1.5$–8.0, it remains unchanged, being 44–45 wt %. The [Cit] : [Bi] ratio in the solid phases increases with an increase in n, achieving a constant value of 1.01 : 1 starging at $n = 1.5$.

The amorphous phases formed in the system below $n = 1.0$ are not of independent interest, because they have no constant composition. Since the [Cit] : [Bi] ratio is always lower than unity, it should be assumed that these phases contain hydroxyl ions along with citrate ions (analysis does not Show NO_3^-).

The main crystalline compound in the system (Fig. 2, curve *1*) with the ratio [Cit] : [Bi] = 1.01 : 1 is not neutral bismuth citrate, as shown by its physicochemical characterization. The sodium percentage in the precipitates was determined as 4.60 wt % (avg.) by chemical analysis and potentiometric titration with the sodium-selective electrode. Thus, the molar ratio [Cit] : [Bi] : [Na] is 1.01 : 1 : 1.05. Recent studies [3, 4], including our works [5, 6], showed that the hydroxyl group of the citrate ion took active part in bonding bismuth in M^I–Bi citrates. The compound formed is a crystal hydrate (Fig. 3). The weight loss in the 60–150°C range is 12.40 wt %. The average chemical analysis results for the isolated compound compared with the calculated data (in parentheses) for $NaBiCit \cdot 3H_2O$ are given below.

Bi – 44.29 (44.00); Cit – 40.49 (39.79);
Na – 4.60 (4.84); H_2O – 12.40 (11.37).

We also obtained a compound of the same composition by reacting bismuth citrate with an aqueous solution of sodium citrate (Fig. 2, curve *2*). It should be mentioned that bismuth citrate is not hydrolyzed in aqueous solutions.

In the temperature range from 300 to 450°C bismuth citrates decomposed to form Bi_2O_3 and gaseous products (Fig. 3). In several cases, metallic bismuth was formed.

Interactions in the $Bi(NO_3)_3$–Na_3Hcit–(H_2O + glycerol) system (equilibrium conditions)

n_{in}	Bi in liquid phase, g-ion/L	pH of equilibrium filtrates	Content in solid phases, wt %		n_s	Composition of compounds
			[Bi]	[C]/[Cit]		
0.25	0.0388	1.21	60.93	13.18/34.60	0.63	Phases of variable composition $Bi(Hcit)_x(OH)_{3(1-x)} \cdot mH_2O$, where $x < 1$*
0.50	0.0190	1.29	56.97	13.56/35.58	0.69	
1.00	0.0038	2.29	52.61	14.88/39.06	0.82	
1.50	0.0005	3.77	44.79	15.42/40.48	1.00	$NaBiCit \cdot 3H_2O$**
2.00	–	4.95	44.20	15.43/40.49	1.01	
2.50	–	5.37	43.96	15.34/40.27	1.01	
4.00	–	5.75	44.22	15.41/40.44	1.01	
6.00	–	5.94	44.29	15.55/40.80	1.01	
8.00	–	6.08	44.29	15.42/40.46	1.01	

n_{in} = [Cit] : [Bi] (mol/mol); n_s = [Cit] : [Bi] (mol/mol) in the solid phases.

Notes: * The presence of sodium in these phases is not excluded but unlikely.

** Sodium was determined in samples: c_{Na}(avg.) = 4.60 wt %.

The IR spectra of sodium bismuth citrate (Fig. 4) exhibit intense bands of asymmetric (ν_{as}(COO) = 1600–1700, 1500 cm^{-1}) and symmetric (ν_s(COO) = 1440 cm^{-1}) vibrations due to the deprotonation of the carboxy-groups (ν(C=O) = 1754, 1692 cm^{-1}) and formation of bonds with metal. The intense narrow absorption band $\nu(OH)_{alc.gr.}$ with a maximum at 3453 cm^{-1} makes the difference between the spectrum of anhydrous neutral bismuth citrate and the spectra of $H_4Cit \cdot H_2O$ and $NaBiCit \cdot 3H_2O$: in the latter, this region contains several overlapping broad absorption bands. The participation of the alcohol group of the citrate ion in bismuth coordination

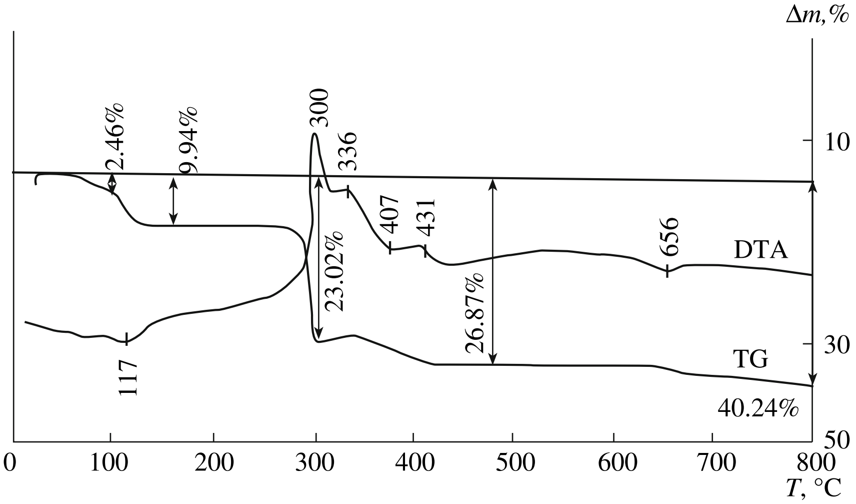

Fig. 3. Thermal curves for $NaBiCit \cdot 3H_2O$.

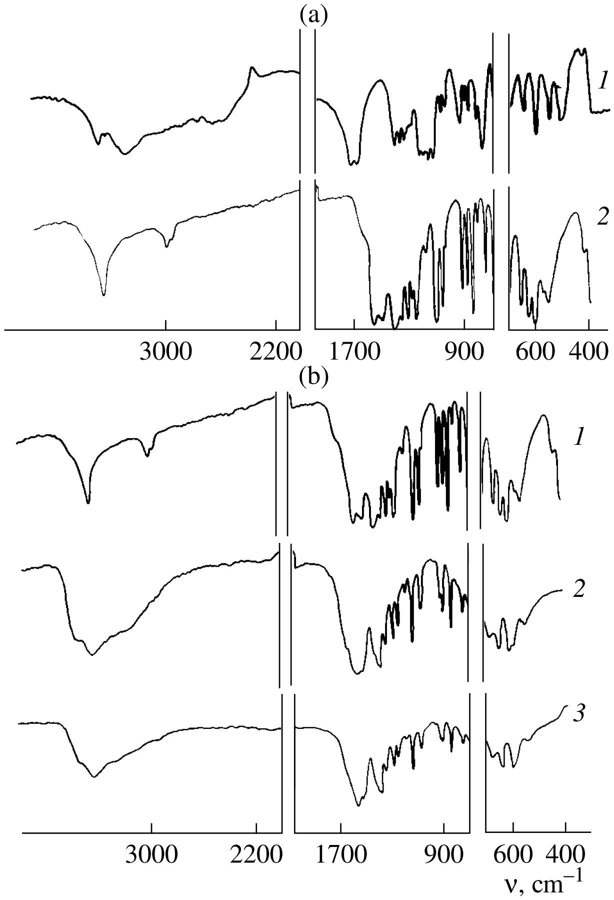

Fig. 4. IR spectra: (a) (*1*) $H_4Cit \cdot H_2O$ and (*2*) BiHcit (anhydrous); (b) (*1*) BiHcit, (*2*) reaction product of BiHcit (anhydrous) and an aqueous solution of $Na_3Hcit \cdot 3H_2O$, and (*3*) $NaBiCit \cdot 3H_2O$ solid phase at the point of the system with *n* = 8.

was proven for double citrates [3–6]. In the absence of structural data for BiHcit, the participation of the OH group in metal coordination cannot be judged about. However, the analysis of the IR and ^{13}C NMR spectra in the solid state [7] suggests that the bond with bismuth occurs only through the atoms of the carboxygroups and the hydroxygroup is not deprotonated.

Thus, the reaction of bismuth nitrate with sodium citrate was studied over a wide interval of component ratios. Aqueous glycerol was proposed to be used instead of aqueous nitric acid solutions to increase the yield of $NaBiCit \cdot 3H_2O$. The composition and physicochemical properties of the reaction products were determined by chemical analysis, X-ray diffraction analysis, DTG, and IR spectroscopy.

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REFERENCES

1. Yu. M. Yukhin, B. B. Bokhonov, T. V. Daminova, et al., *Proceedings of the International Research Conference “Chemistry, Chemical Technology, and Bioengineering at the Turn of the Millenium"* (Tomsk, 2006), Vol. 1, p. 13 [in Russian].
2. Yu. M. Yukhin, Extended Abstract of Doctoral Dissertation in Chemistry (Novosibirsk, 1994).
3. E. Asato, K. Katsura, M. Mikurija, et al., Inorg. Chem. **34**, 2447 (1995).
4. E. Asato and W. L. Driessen, et al., Inorg. Chem. **30**, 4210 (1991).
5. K. K. Palkina, T. B. Kuvshinova, and V. M. Skorikov, Zh. Neorg. Khim. **50** (9), 1461 (2005) [Russ. J. Inorg. Chem. **50** (9), 1357 (2005)].
6. A. S. Antsyshkina, G. G. Sadikov, T. B. Kuvshinova, et al., Zh. Neorg. Khim. **51** (3), 423 (2006) [Russ. J. Inorg. Chem. **51** (5), 374 (2006)].
7. P. J. Barrie, M. I. Djuran, M. A. Mazid, et al., J. Chem. Soc., Dalton Trans., 2417 (1996).