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Melaphen, Malamine, and Bis(hydroxymethyl)phosphinic Acid. Acid–Base Properties and Behavior in the Presence of Some Metal Cations

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Abstract—By means of pH-metry, spectrophotometry, and mathematical modelling of equilibria (CPESSP program) the composition and acid–base properties of melaphen and its components, melamine and bis (hydroxymethyl)phosphinic acid were studied. Bis(hydroxymethyl)phosphinic acid in water solutions is associated by formation of hydrogen bonds and exists as a trimer, and also as the protonated and deprotonated dimeric, trimeric, and tetrameric anionic forms. In the melamine water solutions additionally to the known previously mono-, di-, and triprotonated cations the monoprotonated dimeric particle is found. Interaction of the melaphen components, bis(hydroxymethyl)phosphinic acid and melamine, in water solutions leads to formation of stable formally non-charged particles of the 1:1 and 2:2 composition and the deprotonated associate with 1:1 component ratio. Behavior of the compounds under study in water solutions in the presence of typical complex formers such as the two-charged cations of d-elements and lanthanum(III) is considered. Under the conditions of experiment no noticeable complex formation between melaphen, melamine, and bis (hydroxymethyl)phosphinic acid with cobalt, nickel, copper, zinc, magnesium, and lanthanum was observed. Adequate description of the pH-metric experimental data for the copper(II)-melamine system is achieved by consideration of formation of the hydroxocopper(II) cation. The equilibral processes revealed are characterized quantitatively.

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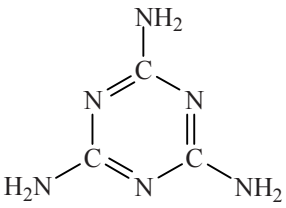
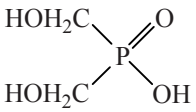
Melamine relates to triazines. It is widely used in the manufacturing of high molecular compounds. Together with bis(hydroxymethyl)phosphinic acid it forms melaphen, the melaminic salt of bis(hydroxymethyl)phosphinic acid, which was synthesized recently [1]. This compound is a regulator of growth and development of plants and is used in agriculture. The protolytic properties of melaphen as well as of bis-(hydroxymethyl)phosphinic acid are not practically studied, and their tendency to participation in complex formation is not considered. Knowledge of such properties seems useful for predicting behavior of these substances in different media. Stable tetramethylammonium, sodium, silver, cobalt, and alkaline earth metals formed by phosphinic acids are known [2]. Reports concerning complex compounds including melamine or melaminium cations are scarce. Nevertheless it was noted by the workers [3] that introduction of cyanuric cycles to the composition of complex compounds seems promising because complex formation can significantly change the properties of ligands. Synthesis of melamine compounds with silver nitrate was reported in 1874 [4]. According to the Liebigs data cooling of hot solution containing melamine and silver nitrate causes the precipitation of white crystals of the compound $C_3H_6N_6AgNO_3$. Its composition does not alter after crystallization. The workers [5] in the course of the pH-potentiometric studies of the lead(II) complex formation with melamine and pyridine-2,6-dicarboxylic acid in the 1:2 ratio in water solutions estab-lished the formation of the binuclear complex with maximum accumulation (α_{max}) 36.1% at pH 3.2. This complex has the same stoichiometry as the compound $(QH_2)_2[Pb_2L_4]$ isolated


(Q)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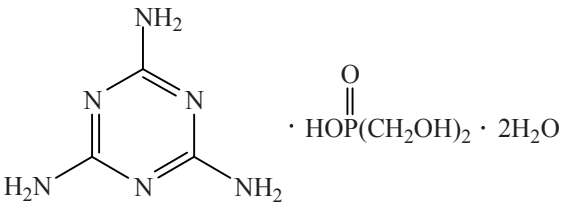
(Q×HA)

in the solid state. Here L^{2-} is the anion of pyridin-2,6-dicarboxylic acid. In this complex the acid anions have intraspheric coordination while the biprotonated melaminium cations form the outer sphere of complex. Besides, in less acidic medium (pH 5.4) has been revealed the compound having the empirical formula $(PbL_2QH)^-$ (α_{max} 68.2%), but the composition of the inner and the outer coordinational spheres were not detailed.

The work presented delivers the results on the condition and protolytic properties of bis(hydroxymethyl)phosphinic acid (HA), melamine (Q), and melaphen (Q×HA) in water solutions. The possibility of interaction of these substances with the series of the bivalent metal ions and lanthanum(III), the typical complex formers, is considered.

Figure 1 presents the curves of pH-metric titration of three compounds under consideration at one and the same concentration. Titration curve of bis(hydroxymethyl)phosphinic acid shows that it is monobasic. pH-metric titration of six bis(hydroxymethyl)phosphinic acid solutions in the concentration range 7.85×10^{-4}–7.85×10^{-2} mol l^{-1} was carried out. Preliminary evaluation of these data (initial pH values of the solutions were used for the estimation of pK_{HA}) showed that bis(hydroxymethyl)phosphinic acid exhibits the middle strength (pK_{HA} –2.20). It occured also that pK_{HA} value depends on the concentration of acid. We proposed that it is connected with the processes of association.

Modelling of all the array of the acid pH-metric titration data showed (Table 1) that in water solutions of bis(hydroxymethyl)phosphinic acid its monomeric form is practically absent. The acid itself exists as a trimer [equilibrium (1)], and in various dimeric, trimeric, and tetyrameric anionic forms [equilibria (2)–(6)] either protonated or deprotonated. Such particles are most probably formed by means of intramolecular hydrogen bonds.

Note that the processes of association take place in water solutions of some other oxygen-containing acids such as orthophosphoric [6], arsenic [7], and monocarboxylic [8] ones. Hence, the fact of association of bis(hydroxymethyl)phosphinic acid established in this work confirms the general tendency of oxygen-containing acids to self-association, and the peculiarity of the acid under investigation revealed through the composition of the polymeric particles formed. Results of modeling the experimental data for the melamine water solution are listed in Table 2. Under the conditions of experiment besides three protonated forms reported about previously [5] the protonated dimeric particle exists in weak acidic medium [equilibrium (9)]. Formation constant only of the monoprotonated form agrees satisfactory with the reported data [5, 9] (Table 2). Reasons of disagreement of constants for the other two forms can hardly be considered because in the report [5] necessary experimental data are absent. Maximum of accumulation of two- and three-protonated forms of melamine reported in that work are low, the error of evaluation of their formation constants must be large. Reported data on the centers of protonation of melamine in melaminium salts are contraversive. Data of the X-ray studies for various

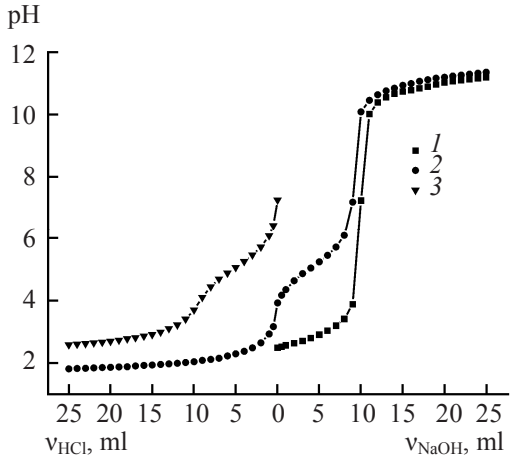

Fig. 1. pH-metric titration curves of the solutions of (*2*) melaphen (Q×HA), (*1*) bis(hydroxymethyl)phosphinic acid (HA), and (*3*) melamine (Q). C_{HA} 3.99×10^{-3}, C_{QHA} 4.0×10^{-3}, C_Q 4.0×10^{-3} mol l^{-1}. C_{HCl} 3.2×10^{-2}, C_{NaOH} 8.0×10^{-3} mol l^{-1}.

Table 1. Equilibria in bis(hydroxymethyl)phosphinic acid solutions

Eq. no.	Equilibrium	log K	α_{max}	pH_{max}
1	$3HA \rightleftarrows (HA)_3$	9.42±0.47	0.12	1.53
2	$4HA \rightleftarrows H^+ + (H_3A_4)^-$	12.19±0.11	0.36	1.53
3	$2HA \rightleftarrows H^+ + (HA_2)^-$	4.62±0.04	0.58	1.87
4	$2HA \rightleftarrows 2H^+ + (A_2)^{2-}$	2.12±0.05	0.82	8.18
5	$3HA \rightleftarrows 3H^+ + (A_3)^{3-}$	4.08±0.26	0.55	7.04

Table 2. Equilibria in melamine solutions

Eq. no.	Equilibrium	log K	α_{max}	pH_{max}
6	$Q + 3H^+ \rightleftarrows (QH_3)^{3+}$	9.27±0.27 6.71 [5]	0.09 0.002 [5]	2.54 2.0 [5]
7	$Q + 2H^+ \rightleftarrows (QH_2)^{2+}$	6.90±0.31 6.02 [5]	0.14 0.06 [5]	2.54 2.0 [5]
8	$Q + H^+ \rightleftarrows (QH)^+$	5.11±0.02 5.22 [5] 5.05 [9] 5.10 [9]	0.95 0.99 [5]	3.39 3.1 [5]
9	$2Q + H^+ \rightleftarrows (Q_2H)^+$	6.92±0.13	0.09	5.14

Table 3. Equilibria in water solutions of melaphen

Eq. no.	Equilibrium	log K	α_{max}	pH_{max}
10	$HA + Q \rightleftarrows QHA$	7.45±0.51	0.25	3.31
11	$2HA + 2Q \rightleftarrows (QHA)_2$	17.54±0.62	0.22	3.92
12	$HA + Q \rightleftarrows (QA)^- + H^+$	2.04±0.21	0.19	6.09
3	$2HA \rightleftarrows H^+ + (HA_2)^-$	4.62	0.43	1.9
4	$2HA \rightleftarrows 2H^+ + (A_2)^{2-}$	2.12	0.68	7.2
5	$3HA \rightleftarrows 3H^+ + (A_3)^{3-}$	4.08	0.25	6.9
6	$Q + 3H^+ \rightleftarrows (QH_3)^{3+}$	9.27	0.15	2.5
7	$Q + 2H^+ \rightleftarrows (QH_2)^{2+}$	6.90	0.14	2.5
8	$Q + H^+ \rightleftarrows (QH)^+$	5.11	0.61	3.4
9	$2Q + H^+ \rightleftarrows (Q_2H)^+$	6.92	0.05	5.1

melaminium salts are tracted by some workers (see for example [10]) in favor of protonation of the heterocyclic nitrogen atom. Another workers [5] on the basis of the same method suggest that the protonation centers are the melamine amino groups in the composition of the outer sphere melaminium cations.

Quantum-chemical calculations carried out by means of the density functional theory method DFT/B3LYP/6-31G(*d,p*) within the frames of the Gaussian 98 program [11] showed that protonation of the imine nitrogen atom in heteroring (Q) is preferred as compared to the protonation of amino group in this compound. Difference in the values of the free energy of formation of the corresponding protonated forms of melamine is 19.2 kcal mol^{-1} (80.3 kJ mol^{-1}) in favor of the first structure.

Consecutive protonation constants for melamine evaluated in the present work are log k_1 5.11, log k_2 1.79, log k_3 2.37. Disagreement with the usual ratio of the consecutive protonation constants log k_1 > log k_2 > log k_3 [12] may be caused by alteration in the protonation center.

Equilibria reflecting the interactions between the components of melaphen solutions are listed in the Table 3. As is seen, in the pH range 2.5–7.2 particles of different composition are present in the melaphen water solutions. In the acidic solutions together with the melaminium cations and the protonated dimeric anion of the acid $(HA_2)^-$ stable formally neutral monomeric and dimeric associates [equilibria (10), (11)] of bis(hydroxymethyl)phosphinic acid and melamine are formed. In the media close to neutral the deprotonated dimeric and trimeric anions of the acid itself prevail. In the weak acidic range (pH ~ 6) the deprotonated (anionic) associate of acid with melamine is formed [equilibrium (12)].

A compound formed by melamine and pyridin-2,6-dicarboxylic acid having the composition analogous to (10) was found in water solution by the workers [5]. But comparison of the stability of these compounds can not be carried out because in water solutions of bis-(hydroxymethyl)phosphinic acid equilibria with participation of the anion A^- are absent.

$$(QA)^- + H^+ \rightleftarrows QHA. \qquad (13)$$

Combination of the expressions (10) and (12) gives the equilibria (13). The constant of this equilibrium log K_{13} = 5.4 with within the evaluation errors coincides with the constant of formation of the

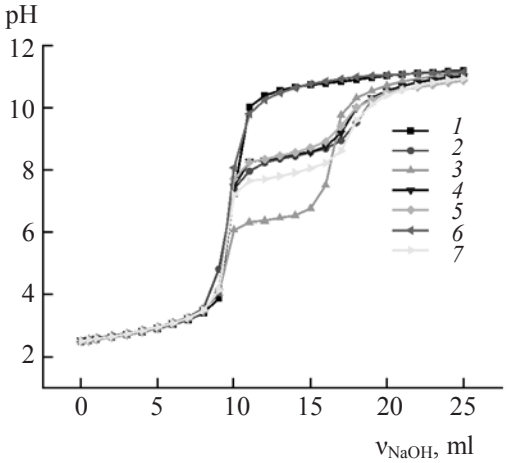

Fig. 2. Curves of the pH-metric titration of the bis(hydroxymethyl)phosphinic acid solutions (C_{HA} 3.99×10^{-3} mol l^{-1}) (*1*) in the absence and (*2*) in the presence of complex formers [C_m $(1.54–1.56)\times10^{-3}$ mol l^{-1}]: (*2*) La(III), (*3*) Cu(II), (*4*) Ni(II), (*5*) Co(II), (*6*) Mg(II), and (*7*) Zn(II). C_{NaOH} 7.95×10^{-3} mol l^{-1}.

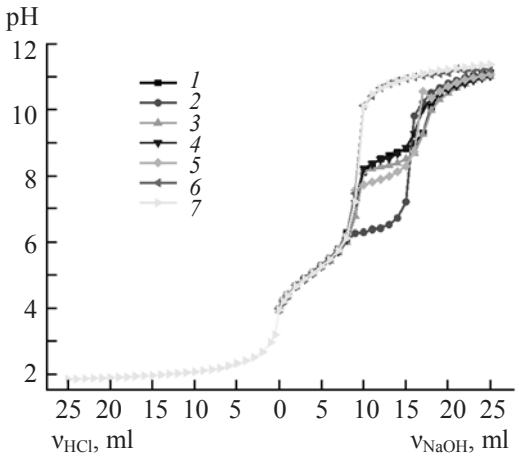

Fig. 3. Curves of the pH-metric titration of melaphen solutions (C_{QHA} 4.0×10^{-3} mol l^{-1}) (*1*) in the absence and (*2*) in the presence of complex formers [C_m $(1.54–1.56)\times10^{-3}$ mol l^{-1}]: (*2*) La(III), (*3*) Cu(II), (*4*) Ni(II), (*5*) Co(II), (*6*) Mg(II), and (*7*) Zn(II). C_{HCl} 3.2×10^{-2} mol l^{-1}, C_{NaOH} 7.95×10^{-3} mol l^{-1}.

monoprotonated form of melamine $(QH)^+$ (log K_S 5.11) (Table 2). In other words melamine holds proton with practically the same strength as its associate with the bis(hydroxymethyl)phosphinic acid anion.

Association is provided by H-bonds and the electrostatic interactions. High stability of the dimeric compound may be explained additionally by the π–π-stacking interaction [13].

Further we shall consider the behavior of all three compounds under study in the presence of the metal cations. Introduction of salts of the bivalent metals such as copper, cobalt, nickel, zinc, magnesium, and also lanthanum(III) to the solutions of bis(hydroxymethyl)phosphinic acid does not cause their acidifying as compared to those containing no complex formers. As the acid is considerably strong, its possible interaction with complex formers under study is not registered by the pH metering. Coloration of the acid solutions containing copper(II), cobalt(II) or nickel(II) does not differ visually from the coloration of solutions containing corresponding aquaions.

Titration curves of the acid in presence of complex formers (Fig. 2) in the pH range 2.5–6 practically coincide with the titration curve for acid by itself. At the achievement of the solubility product [14], the basic salts and hydroxides of corresponding metals pre-cipitate. The only exclusion is magnesium(II). Titra-tion curves of the pure acid (*1*) and of the acid in the presence of the magnesium salt (*6*) practically coincide because under the conditions of experiment the value of the solubility product for the magnesium hydroxide is not achieved.

Analogous effects are observed for the melaphen solutions in the presence of copper(II), cobalt(II), and nickel(II). No alterations in coloration is observed, and precipitates are not formed at the acidifying solutions. pH values of the melaphen solutions in the absence and in the presence of copper(II) in different concentrations practically coincide. That is why the melaphen solutions containing metal cations were titrated with alkali (Fig. 3). Here as in the case of bis (hydroxymethyl)phosphinic acid at the achievement of the solubility product the basic salts and metal hydroxides precipitate. Hence, melaphen as well as bis-(hydroxymethyl)phosphinic acid does not form intraspheric complexes with the above-considered metal cations.

The melamine solutions behave differently. Some decrease in the pH of melamine solutions containing metal cations is observed. In the case of Cu(II) this decrease is equal practically to one Ph unit (7.23 and 6.19, respectively at different ratio of melamine and copper(II) concentrations. The facts marked may be related either a result of the reaction of copper(II) with melamine or they may be caused by the hydrolysis of copper(II) aquacomplex. But no distinct changes in the

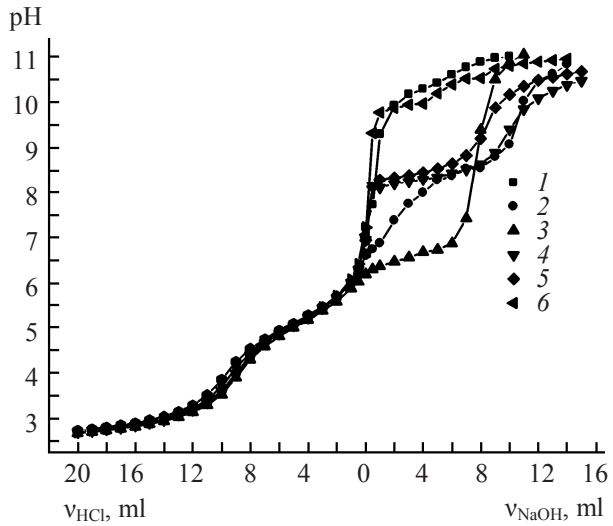

Fig. 4. Curves of the pH-metric titration of the melamine solutions (C_Q 1.5×10^{-3} mol l^{-1}) (*1*) in the absence and (*2*) in the presence of complex formers [C_m 1.5×10^{-3} mol l^{-1}]: (*2*) La(III), (*3*) Cu(II), (*4*) Ni(II), (*5*) Co(II), and (*6*) Mg(II). C_{NaOH} 7.95×10^{-3}, C_{HCl} 3.2×10^{-2}.

coloration of solutions were observed. Broad band of moderate intensity (ε_{780} = 16 l mol^{-1} cm^{-1}) in the range 600–850 nm in the electron absorption spectrum of melamine solutions containing copper(II) coincides practically with the absorption band of copper(II) aquacomplex. Melamine itself (C_Q = 4.0×10^{-3} mol l^{-1}, pH 7.25) absorbs in the UV part of spectrum (ε_{191} = 250 and ε_{242} = 910 l mol^{-1} cm^{-1}).

Mathematical modeling of corresponding pH-metric experimental data (Fig. 4) showed that maximum part of accumulation of copper(II) complex with melamine of the 1:2 composition is negligibly small (α_{max} = 2.42%). Adequate description (Table 4) is achieved by addition of the stage of hydrolysis of copper(II) aquacomplex in the stoichiometry matrix [equilibrium (14)]. Hence, neither melaphen nor its components are capable of formation of the intraspheric complexes with typical complex formers.

Table 4. ces in water solutions of melamine containing copper (II)

Eq. no.	Equilibrium	log *K*	α_{max}	pH_{max}
8	$Q + H^+ \rightleftarrows (QH)^+$	4.98±0.05	0.98	3.03
9	$2Q + H^+ \rightleftarrows (Q_2H)^+$	7.16±0.43	0.15	4.99
14	$Cu^{2+} + HOH \rightleftarrows (CuOH)^+ + H^+$	–6.73±0.43	0.22	6.18

EXPERIMENTAL

The work presented was carried out by means of the pH-metric titration and partially by means of spectrophotometry. pH values of the solutions were measured on a pH-673 M device. ELS-43-07 glass electrode was used as the indicator, and the saturated silver chloride electrode was used as a reference one. Electron absorption spectra of the solutions were taken against water on a Perkin-Elmer Lambda EZ210 spectrophotometer in 1 cm quartz cuvettes.

Bis(hydroxymethyl)phosphinic acid was synthesized according to [15], and melaphen, according to [1]. Melamine was of the "chemically pure" grade. Concentration of starting bis(hydroxymehyl)phosphinic acid solution was established by means of the pH-metric titration and volumetric analysis. The melamine and melaphen solutions were prepared by means of the precisely weight samples. The studies were carried out with water solutions. Ionic force of solutions was created by means of its components because introduction of the background electrolyte decreases the solubility of compounds and may affect the processes of association in solution. The ionic force varied within the range 0.006–0.02. Working solutions of the carbonate-free sodium hydroxide, hydrochloric acid, copper(II), lanthanum(III), cobalt (II) nitrates and nickel(II), magnesium(II), and zinc(II) sulfates were prepared from the commercial products of the "chemically pure" grade. Concentrations of operating solutions were established volumetrically.

In the course of the experiment bis(hydroxymethyl) phosphinic acid solutions were titrated pH-metrically with sodium hydroxide solutions, the melamine solutions were titrated with hydrochloric acid, and the melaphen solutions with the solutions of acid and alkali. Titration with the constant addition of titrants was carried out in the thermostated glass cell (298 K). In the course of investigation of complex formation the titrated solutions contained additionally copper(II), nickel(II), cobalt(II), zinc(II), magnesium(II), or lanthanum(III). The solutions titrated were stirred with the magnetic stirrer.

Reproducible values of the glass electrode potentials were reached in the course of 2–3 min, but in the range close to the equivalence point this time increased significantly. In this case pH values were measured 10 min after the addition of the next portion of titrant.

Experimental data were treated by means of the CPESSP program [16]. In the course of mathematical modeling of protolytic equilibria or the reactions of complex formation on the basis of the pH-metric data within the frames of the CPESSP data [16] value of the Bierrum formation function $\bar{n}$ [17] depending on the pH of solutions was used as the modeled response. Average part of deviations of the experimental data from the calculated one (*R* factor [18]) was not more than 5%.

Quantum-chemical calculations were carried out with Gaussian-98 packege program [11] by means of the density functional method B3LYP/6-31G(d,p) with the complete optimization of geometry of melaminium cations without the symmetry limitations. Correspondence of the considered structures to the energy minimum point was checked by calculation of the Hesse martix (all frequencies in it are positive).

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