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SUPPORTING INFORMATION

Title: Aminoalkylbis(phosphonates): Their Complexation Properties in Solution and in the Solid State
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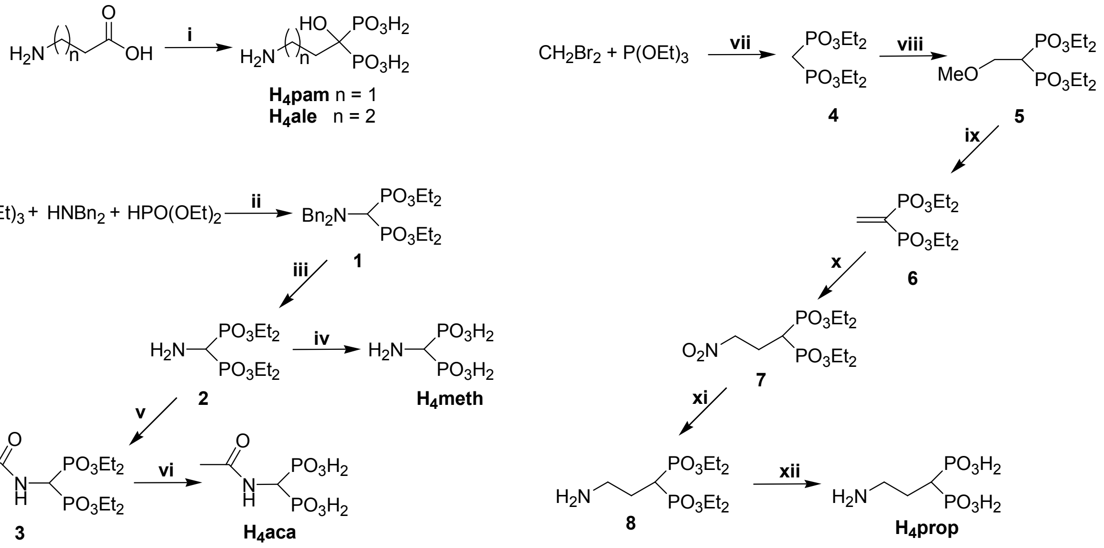
Ref. No.: I200600615

Synthesis

Discussion

Scheme S1. Syntheses of the ligands. i) 1) H_3PO_3, PCl_3, $MeSO_3H$, 65 °C; 2) water, reflux; ii) 160 °C; iii) H_2, Pd/C, EtOH, reflux; iv) 6 M HCl, reflux; v) $CH_3C(O)Cl$, acetonitrile, Na_2CO_3, –40 °C; vi) 30 % HBr/AcOH, RT; vii) 150 °C; viii) MeOH, CH_2O, $NHEt_2$, reflux; ix) p-toluenesulfonic acid, toluene, reflux; x) $MeNO_2$, NaH, THF, RT; xi) H_2, Pd/C, EtOH, reflux; xii) 6 M HCl, reflux



Ligands H_4pam (ref.[1]), H_4ale (ref.[1]), H_4meth (ref.[2]) and H_4prop (ref.[3]) were prepared by modification of reported procedures. Hydroxy-bis(phosphonates) H_4pam and H_4ale can be prepared in one step from commercially available aminocarboxylic acids (Scheme S1). The low yields of these reactions (25 % and 56 %, not optimized) are fully compensated by a simple isolation of the pure products. Syntheses of other ligands require multi-step procedures (Scheme S1).

Formation of aminomethyl-bis(phosphonate) fragment occurs in one step by reaction of triethylorthoformate, dibenzylamine and diethylphosphite. The low yield and a presence of many by-products make chromatografic purification of the dibenzyl derivative **1** complicated. Debenzylation with H_2/Pd/C followed by hydrolysis of ester groups in azeotropic hydrochloric acid yields ligand H_4meth almost quantitatively. Tetraethyl aminomethyl-bis(phosphonate) **2** was converted quantitatively into compound **3** by means of a substitution reaction with an excess of acetylchloride. After deesterification in a solution of HBr in dry AcOH, ligand H_4aca was crystallized from water by diffusion of organic solvent as an adduct with THF. Arbuzov reaction of dibromomethane with triethylphosphite results in tetraethyl methylenebis(phosphonate) **4** in a high yield. The two-step preparation of vinylidene-bis(phosphonate) **6** can be performed without isolation of the methoxy intermediate **5** in a high yield. Further addition of nitromethane anion to the

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vinylidene-bis(phosphonate) **6** gives nitroderivative **7**. As compound **7** can react with another molecule of vinylidene-bis(phosphonate) **6**, double-substituted product (observed also in the original paper[3]) is present in the reaction mixture. This can be easily removed by a column chromatography. During reduction of the nitro group, compound **8** undergoes a slow decomposition and several by-products were formed. Therefore, a careful control of the reaction time by ^{31}P NMR is necessary to assure a high yield of the synthesis. The final hydrolysis of ester groups proceeds quantitatively and ligand H$_4$prop was obtained in a high yield.

Experimental Section

ω-Aminoalkyl-1-hydroxy-1,1-bis(phosphonic acid) (H$_4$pam and H$_4$ale) – General Procedure[1]

Appropriate ω-aminocarboxylic acid (85.4 mmol) and H_3PO_3 (7.0 g, 85.4 mmol) were dissolved in methanesulfonic acid (33 mL) and heated at 65 °C. PCl_3 (24.7 g, 180 mmol) was added dropwise with vigorous stirring and the mixture was heated at 65 °C overnight. The resulting solution was poured into water (150 mL) and the mixture was refluxed for 8 h. After cooling at RT, EtOH (350 mL) was added. After 12 h, the crystals were collected by filtration, washed with water, EtOH and dried *in vacuo* at 80 °C.

3-Aminopropyl-1-hydroxy-1,1-bis(phosphonic acid) (H$_4$pam)

Yield 5.0 g (25 %). Anal. Calcd. for $C_3H_{11}NO_7P_2$: C, 15.33; H, 4.72; N, 5.96. Found: C, 15.36; H, 4.90; N, 6.00. ^{1}H NMR (D_2O/NaOD): $\delta = 1.82$ (m, 2H, CH_2–CH_2–C), 2.70 (t, 2H, –CH_2–NH_2, $^3J_{HH} = 8.0$ Hz) ppm. ^{31}P NMR (D_2O/NaOD): $\delta = 21.7$ (t, $^3J_{HP} = 32.0$ Hz) ppm. ESI/MS: calculated 258.1, observed 257.9 (M+Na$^+$).

4-Aminobutyl-1-hydroxy-1,1-bis(phosphonic acid) (H$_4$ale)

Yield 12.1 g (56 %). Anal. Calcd. for $C_4H_{13}NO_7P_2$: C, 19.29; H, 5.26; N, 5.62. Found: C, 19.55; H, 5.05; N, 5.48. ^{1}H NMR (D_2O/NaOD): $\delta = 1.6$–1.9 (m, 4H, CH_2–CH_2–CH_2–C), 2.52 (t, 2H, –`CH_2–NH_2, $^3J_{HH} = 6.8$ Hz) ppm. ^{31}P NMR (D_2O/NaOD): $\delta = 21.9$ (t, $^3J_{HP} = 32.0$ Hz) ppm. ESI/MS: calculated 272.1, observed 272.0 (M+Na$^+$).

Tetraethyl (*N*,*N*-dibenzyl)aminomethyl-bis(phosphonate) (1)[2]

Triethyl orthoformate (10.6 g, 71 mmol), diethyl phosphite (25.6 g, 186 mmol) and dibenzylamine (11.8 g, 59.9 mmol) were mixed in a 100 mL three-necked round bottom flask. The solution was refluxed under argon atmosphere (150 °C in an oil bath). After 5 h, the cooler was removed and the solution was heated for 24 h at 160 °C under argon flux to remove the ethanol. After cooling to RT, $CHCl_3$ (300 mL) was added and the solution was washed with 3×60 mL of 5 % aq. NaOH and 2×75 mL of brine. The organic phase was dried with anhydrous Na_2SO_4 and the solvent was removed by rotary evaporation. The resulting oil was purified by column chromatography on silica gel (6x20 cm) (hexane:EtOH, from 100:0 to 0:100). Yield 12.4 g (43 %) of viscous, colourless oil. R_f (hexane:EtOAc, 1:1) = 0.2–0.3. ^{1}H NMR ($CDCl_3$): $\delta = 1.32$ (td, 12H, –CH_3, $^3J_{HH} = 7.2$ Hz, $^4J_{PH} = 2.0$ Hz), 3.55 (t, 1H, P–CH–P, $^2J_{PH} = 25.2$ Hz), 4.07 (m, 4H, N–CH_2–Ph), 4.15 (m, 8H, O–CH_2–), 7.20–7.45 (m, 10H, Ar–*H*) ppm. ^{31}P NMR ($CDCl_3$): δ = 20.7 (d, $^2J_{HP}$ = 25.2 Hz) ppm. ESI/MS: calculated 506.5, observed 506.7 ($M+Na^+$).

Tetraethyl aminomethyl-bis(phosphonate) (2)[2]

A 250 mL three-necked round bottom flask was flushed with argon, charged with 10 % Pd/C (0.8 g) and then a solution of **1** (4.0 g, 8.3 mmol) in anhydrous EtOH (150 mL) was added. The mixture was vigorously stirred at 70 °C under hydrogen atmosphere for 24 h. After filtration of the solids and evaporation of volatiles, the product was obtained as colourless oil. Yield 2.4 g (96 %). ^{1}H NMR ($CDCl_3$): δ = 1.36 (t, 12H, –CH_3, $^3J_{HH}$ = 6.8 Hz), 3.43 (t, 1H, P–C*H*–P, $^2J_{PH}$ = 20.4 Hz), 4.23 (m, 8H, O–CH_2–) ppm. ^{31}P NMR ($CDCl_3$): δ = 20.8 (d, $^2J_{HP}$ = 20.4 Hz) ppm. ESI/MS: calculated 326.2, observed 326.2 ($M+Na^+$).

Aminomethyl-bis(phosphonic acid) (H_4meth)[2]

A solution of **2** (3.0 g, 9.9 mmol) in 6 M HCl (50 mL) was refluxed overnight. After cooling to room temperature, the precipitate formed was collected by filtration, washed with water, EtOH and dried *in vacuo* at 60 °C. Yield 1.8 g (95 %). Anal. Calcd. for $CH_7NO_6P_2$: C, 6.29; H, 3.69; N, 7.33. Found: C, 6.11; H, 3.73; N, 7.39. ^{1}H NMR (D_2O/NaOD): δ = 2.68 (t, $^2J_{PH}$ = 17.5 Hz) ppm. ^{31}P NMR (D_2O/NaOD): δ = 16.9 (d, $^2J_{HP}$ = 17.5 Hz) ppm. ESI/MS: calculated 214.0, observed 213.8 ($M+Na^+$).

Tetraethyl acetamidomethyl-bis(phosphonate) (3)

A solution of **2** (4.0 g, 13.2 mmol) in dry acetonitrile (50 mL) was added dropwise into a solution of acetylchloride (3.0 g, 38.2 mmol) with suspended Na_2CO_3 (5.2 g, 49 mmol) in dry acetonitrile (50 mL) at –40 °C. After the addition was finished, the mixture was allowed to warm slowly to room temperature and stirred overnight. After treatment with charcoal and filtration, the excess of acetylchloride was removed by repeated vacuum evaporation with toluene. The product was obtained as colourless oil in yield of 4.4 g (97 %). Anal. Calcd. for $C_7H_{17}NO_8P_2$: C, 29.28; H, 5.27; N, 4.88. Found: C, 29.42; H, 5.41; N, 4.25. ^{1}H NMR ($CDCl_3$): δ = 1.34 (m, 12H, CH_2–CH_3), 2.08 (s, 3H, CH_3–CO), 4.19 (m, 8H, O–CH_2–), 5.06 (td, 1H, P–C*H*–P, $^2J_{PH}$ = 21.4 Hz, $^3J_{HH}$ = 10.4 Hz), 6.75 (bs, 1H, –N*H*) ppm. ^{31}P NMR ($CDCl_3$): δ = 17.0 (d, $^2J_{HP}$ = 21.4 Hz) ppm. ESI/MS: calculated 368.3, observed 368.3 ($M+Na^+$).

Acetamidomethyl-bis(phosphonic acid) (H_4aca)

In 100 mL flask, the compound **3** (3.0 g, 8.7 mmol) was dissolved in 30 % HBr/AcOH (50 mL) and stirred for 24 h at room temperature. After removal of volatiles on a rotary evaporator, the resulting oil was dissolved in EtOH (30 mL). From the solution, a precipitation of crude product occurred on standing. After 3 h, the precipitate was filtered off and extracted with boiling EtOH (100 mL). After filtration with charcoal, volatiles were removed in vacuum. The crude product was recrystallized from water by addition of THF. The product was filtered, washed with THF and dried at room temperature over P_2O_5. Yield 1.7 g (63 %) as adduct **H₄aca**·THF. Anal. Calcd. for $C_7H_{17}NO_8P_2$: C, 27.55; H, 5.61; N, 4.59. Found: C, 27.62; H, 5.60; N, 4.35. ^{1}H NMR (D_2O/NaOD): δ = 1.94 (s, 3H, CH_3–CO), 4.46 (t, 1H, P–C*H*–P, $^2J_{PH}$ = 21.3 Hz) ppm. ^{31}P NMR (D_2O/NaOD): δ = 17.0 (d, $^2J_{HP}$ = 21.3 Hz) ppm. ESI/MS: calculated 256.0, observed 255.8 (M+Na$^+$).

Tetraethyl methylene-bis(phosphonate) (4)

250 mL three-necked flask equipped with thermostatted condenser was flushed with argon and charged with dibromomethane (100 g, 0.53 mol) and triethylphosphite (400 g, 2.41 mol). Resulting mixture was heated at 150 °C for 5 days under gentle stream of argon, while water in the cooler was maintained at 45 °C to allow a removal of ethylbromide. Vacuum distillation afforded product as colourless oil (b.p. 96–100 °C/0.1 mbar). Yield 130.4 g (85 %). ^{1}H NMR ($CDCl_3$): δ = 1.36 (t, 12H, –CH_3, $^3J_{HH}$ = 7.2 Hz), 2.45 (t, 2H, P–CH_2–P, $^2J_{PH}$ = 20.8 Hz), 4.19 (m, 8H, O–CH_2–) ppm. ^{31}P NMR ($CDCl_3$): δ = 19.8 (m) ppm. ESI/MS: calculated 311.2, observed 311.0 (M+Na$^+$).

Tetraethyl vinylidene-1,1-bis(phosphonate) (6)[3]

In 1000 mL round-bottom flask, the compound **4** (23.5 g, 81 mmol) was mixed with paraformaldehyde (12.5 g, 0.42 mol), diethylamine (6 g, 82 mmol) and dissolved in 235 mL of MeOH. Mixture was refluxed overnight and the volatiles were removed by rotary evaporation and traces of MeOH were removed by co-distillation with toluene. Resulting methoxy intermediate **5** was dissolved in toluene (200 mL) and *p*-toluenesulfonic acid monohydrate (0.5 g, 2.6 mmol) was added. Solution was refluxed overnight and volatiles were removed by rotary evaporation. Vacuum distillation yielded product as colourless oil (b.p. 80–83 °C/0.05 mbar). Yield 20.6 g (94 %). ^{1}H NMR ($CDCl_3$): δ = 1.18 (t, 12H, –CH_3, $^3J_{HH}$ = 7.2 Hz), 3.98 (m, 8H, O–CH_2–), 6.82 (m, 2H, C=CH_2) ppm. ^{31}P NMR ($CDCl_3$): δ = 11.3 (m) ppm. ESI/MS: calculated 323.2, observed 323.4 (M+Na$^+$).

Tetraethyl 3-nitropropyl-1,1-bis(phosphonate) (7)[3]

100 mL three-necked flask was flushed with argon and charged with NaH (54 mg, 2.3 mmol) and dry tetrahydrofurane (20 mL). Nitromethane (21.6 g, 0.35 mol) was added dropwise to the stirred suspension. After 1 h, the compound **6** (3.0 g, 10.0 mmol) was added in one portion and the mixture was stirred for 3 days at RT. After evaporation of volatiles, the resulting oil was purified by column chromatography on silica gel (EtOAc:EtOH, 3:1). Yield 3.0 g (83 %) of viscous colourless oil. R_f (EtOAc:EtOH, 3:1) = 0.8–0.9. ^{1}H NMR ($CDCl_3$): δ = 1.36 (td, 12H, –CH_3, $^3J_{HH}$ = 7.2 Hz, $^4J_{PH}$ = 1.2 Hz), 2.4–2.7 (m, 3H, CH_2–C*H*–), 4.21 (m, 8H, O–CH_2–), 4.72 (t, 2H, –CH_2–NO_2, $^3J_{HH}$ = 6.8 Hz) ppm. ^{31}P NMR ($CDCl_3$): δ = 19.0 (m) ppm. ESI/MS: calculated 384.3, observed 384.0 (M+Na$^+$).

Tetraethyl 3-aminopropyl-1,1-bis(phosphonate) (8)[3]

A 250 mL two-necked round bottom flask was flushed with argon, charged with 10 % Pd/C (0.6 g) and then a solution of **7** (6.0 g, 16.6 mmol) in anhydrous EtOH (150 mL) was added. The mixture was vigorously stirred at 70 °C under hydrogen atmosphere for 24 h. After filtration of the solids and evaporation of volatiles, the resulting oil was purified by column chromatography on silica gel (NEt_3:MeOH:H_2O, from

0:100:100 to 4:100:100). Yield 3.4 g (62 %) of viscous, colourless oil. R_f (NEt_3:MeOH:H_2O, 2:100:100) = 0.3–0.4. ^{1}H NMR ($CDCl_3$): δ = 1.28 (t, 12H, –C*H*$_3$, $^3J_{HH}$ = 7.2 Hz), 2.02 (m, 2H, CH_2–C*H*$_2$–CH), 2.52 (tt, 1H, P–C*H*–P, $^3J_{HH}$ = 6.4 Hz, $^2J_{PH}$ = 24.0 Hz), 2.85 (bs, 2H, –N*H*$_2$), 2.91 (t, 2H, –C*H*$_2$–NH_2, $^3J_{HH}$ = 7.2 Hz), 4.12 (m, 8H, O–C*H*$_2$) ppm. ^{31}P NMR ($CDCl_3$): δ = 21.9 (m) ppm. ESI/MS: calculated 354.3, observed 354.1 (M+Na^+).

3-Aminopropyl-1,1-bis(phosphonic acid) (H_4prop)

A solution of **8** (3.0 g, 9.1 mmol) in 6 M HCl (100 mL) was refluxed overnight. After cooling to room temperature, volatiles were removed by rotary evaporation and the resulting oil was dissolved in water (10 mL). After 12 h, the precipitate was filtered, washed with water, EtOH and dried *in vacuo* at 80 °C. Yield 1.8 g (93 %). Anal. Calcd. for $C_3H_{11}NO_6P_2$: C, 16.45; H, 5.06; N, 6.39. Found: C, 16.60; H, 5.03; N, 6.22. ^{1}H NMR (D_2O/NaOD): δ = 1.45 (tt, 1H, P–C*H*–P, $^3J_{HH}$ = 6.0 Hz, $^2J_{PH}$ = 22.0 Hz), 1.75 (m, 2H, CH_2–C*H*$_2$–CH), 2.65 (t, 2H, –C*H*$_2$–NH_2, $^3J_{HH}$ = 7.6 Hz) ppm. ^{31}P NMR (D_2O/NaOD): δ = 23.9 (m) ppm. ESI/MS: calculated 242.1, observed 242.0 (M+Na^+).

Figure S1

Fitting of the experimental data of the Na(I):H_4prop system. Experimental points (dots), fit including hydroxospecies (blue; the sum of squares of residuals was 5614), fit without hydroxospecies (red; the sum of squares of residuals was 41136).

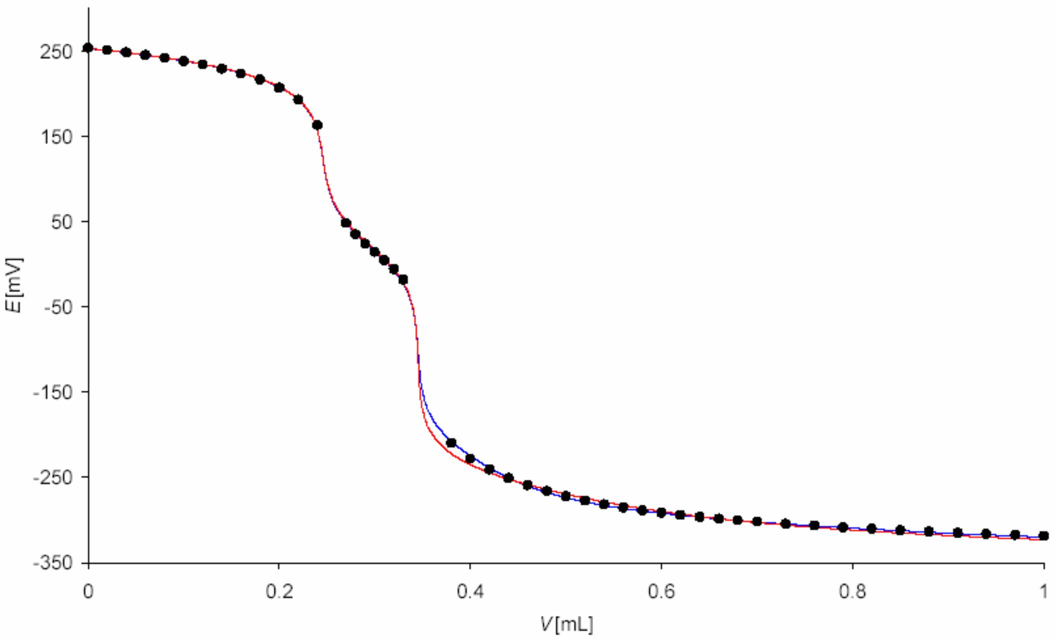

Table S1

pH ranges skipped during titration due to the precipitate formation

metal ion	L:M ratio	H_4pam	H_4ale	H_4meth	H_4aca	H_4prop
Cu(II)	1:1	2.8-5.9	2.8-5.8	[a]	5.2-9.8	3.8-10.3
	2:1	3.7-6.3	3.7-6.3	[a]	5.6-10.4	6.9-10.3
	1:2	2.8-9.8	2.8-9.8	[a]	2.9-10.0	3.5-10.6
Zn(II)	1:1	3.4-9.5	3.4-9.5	2.4-10.8	2.9-10.7	3.2-10.1
	2:1	3.2-10.0	3.2-10.0	2.6-9.1	3.0-10.6	3.0-10.3
	1:2	2.8-10.9	2.8-10.9	[a]	3.4-11.5	3.2[b]
Ca(II)	1:1	[a]	3.8-10.8	[a]	[a]	6.1-11.2
	2:1	[a]	3.3-10.5	[a]	[a]	6.5-10.9
	1:2	[a]	3.3-11.8	[a]	[a]	5.8[b]
Mg(II)	1:1	5.8-10.9	5.8-10.9	3.3-10.5	3.0-10.9	7.6-10.7
	2:1	6.8-10.2	6.8-10.2	3.2-8.4	3.1-10.4	7.1-9.9
	1:2	5.6-11.4	5.6-11.4	[a]	3.3-10.6	6.8[b]

[a] System was not studied due to an excessive precipitate formation.

[b] System was studied only in acidic region as a precipitate does not dissolve at alkaline solution.

Table S2

Comparison of the determined dissociation constants pK_a with those reported in literature.

Species	H_4pam			H_4ale				H_4meth			
	[a]	ref. 4[b]	ref. 5[f]	[a]	ref. 4[b]	ref. 6[d]	ref. 7[e]	[a]	ref. 8[b]	ref. 9[c]	ref. 10[e]
HL^{3-}	13.06	10.8	>12	12.68	11.6	~12	12.04	11.43	10.42	11.72	11.03
H_2L^{2-}	10.30	9.9	9.36	11.07	10.5	10.79	10.77	8.29	8.06	8.42	8.85
H_3L^{-}	5.85	5.83	5.72	6.36	8.73	6.36	6.21	5.35	5.59	5.42	5.18
H_4L	1.80	2.55	1.8	2.19	2.72	2.38	2.16	1.18	1.7	1.4	1.5
H_5L^{+}	<1.2			<1.2		~1	~1	<1.2			<1.0

[a] This work; [b] 0.1M KCl; [c] 0.1 M NMe_4NO_3; [d] 0.1 M KNO_3; [e] 0.2 M KCl; [f] 1.0 M KNO_3

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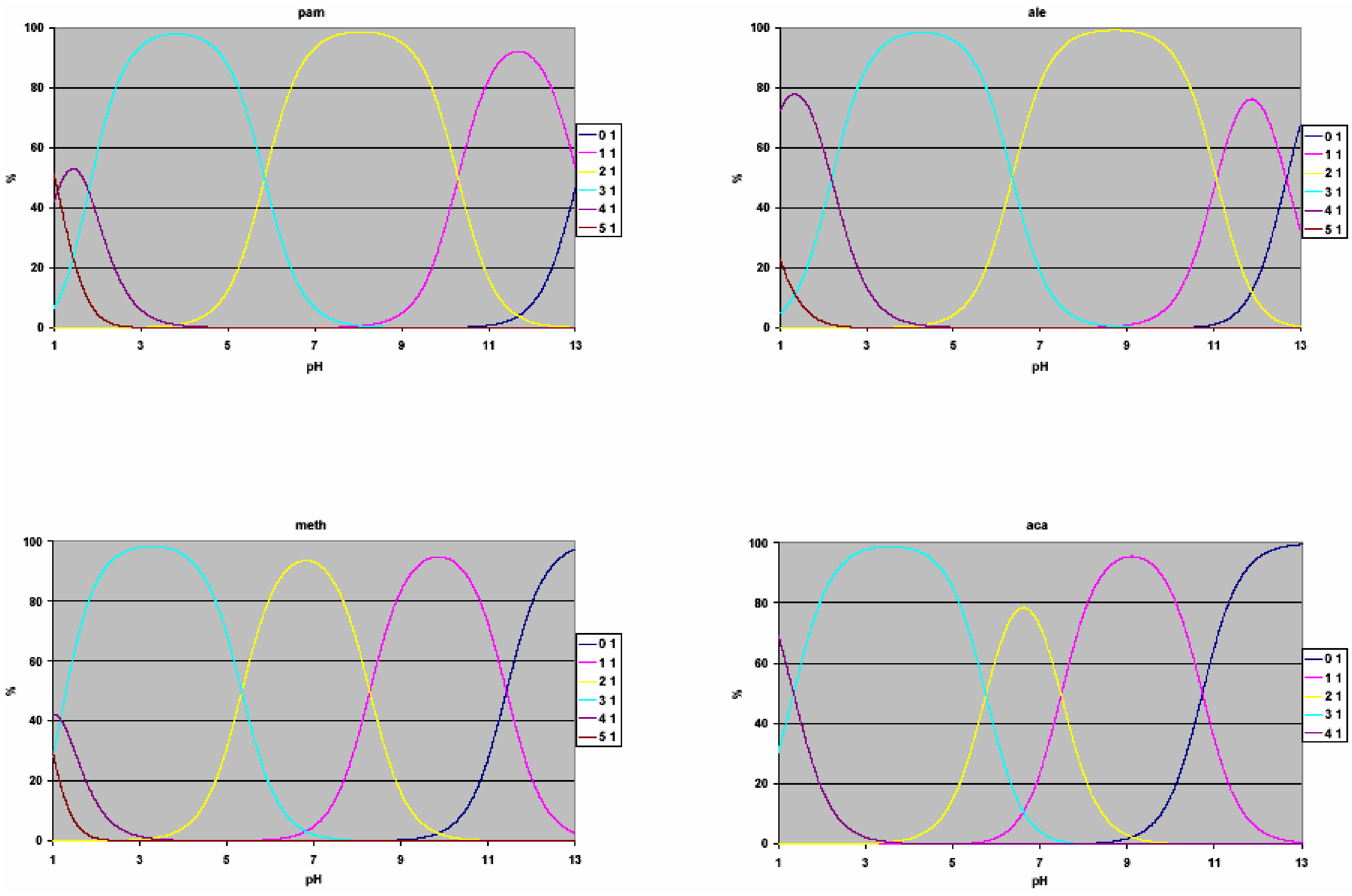
Figure S2

Distribution diagrams of free ligands (abundance of the ligand on the y axis)



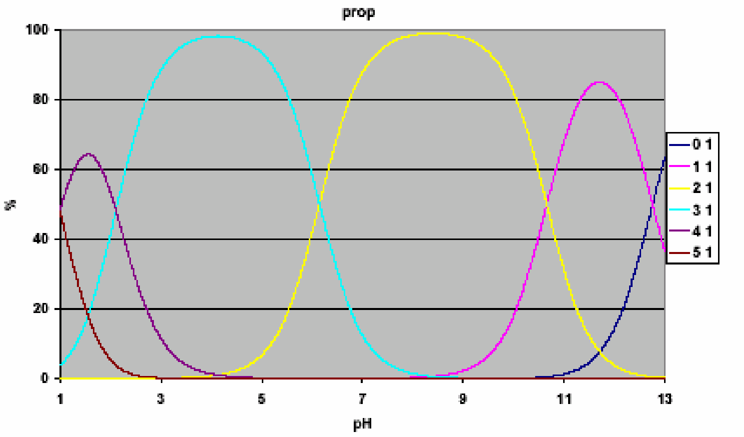

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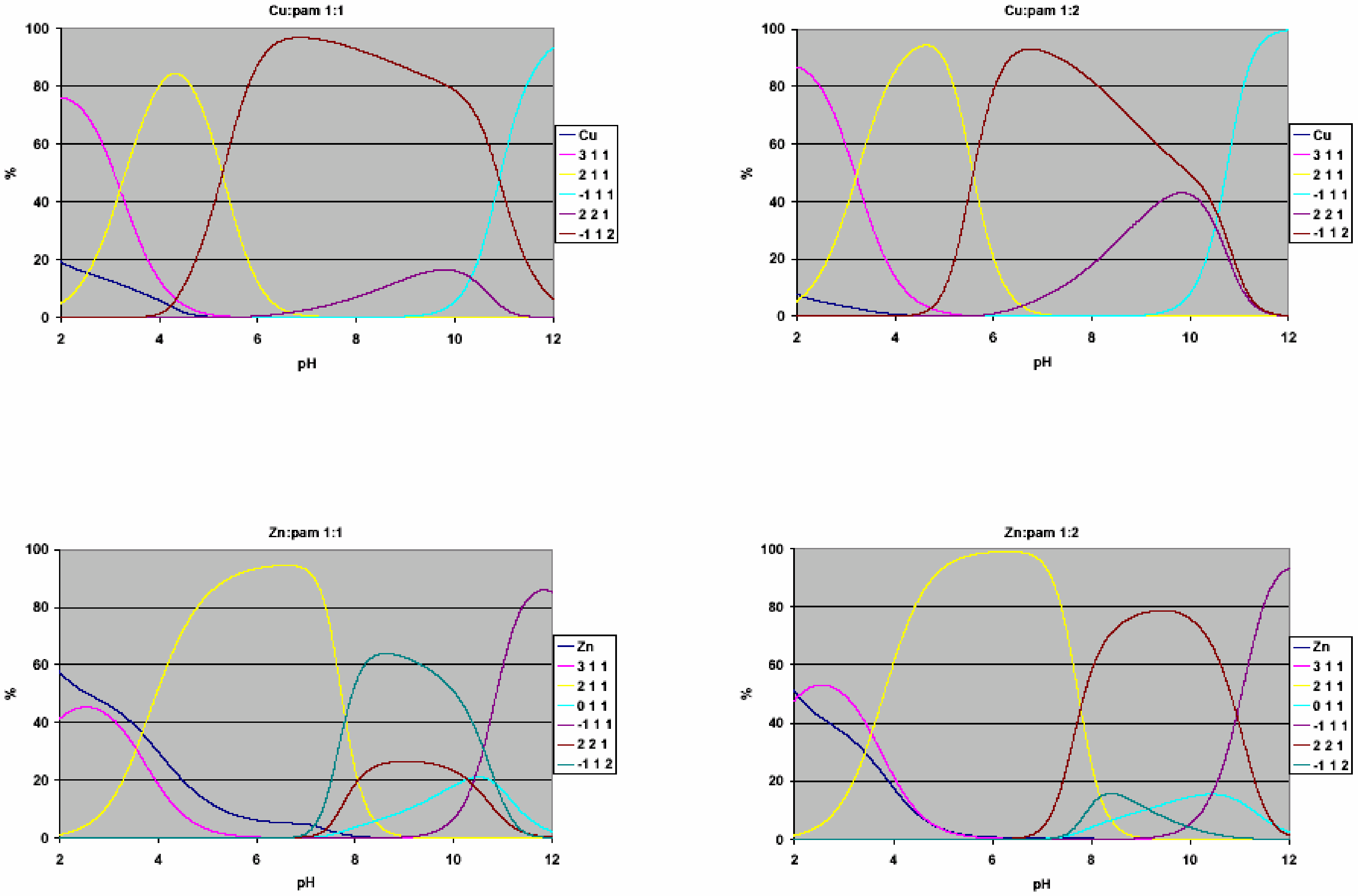
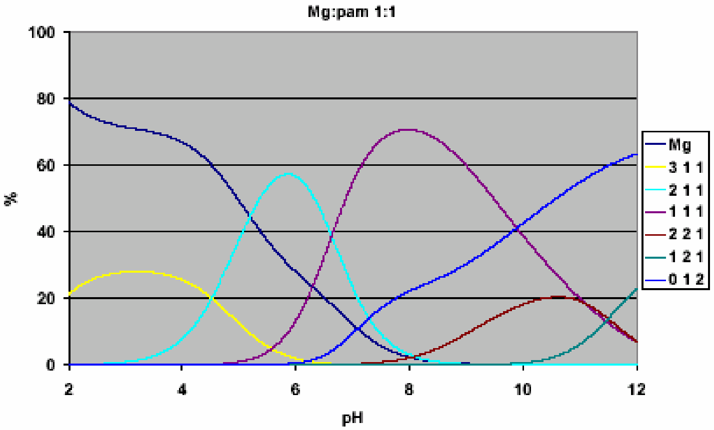
Figure S3

Distribution diagrams of metal:H_4pam systems (abundance of the metal ions on the y axis, for pH region with precipitates see Table S1)

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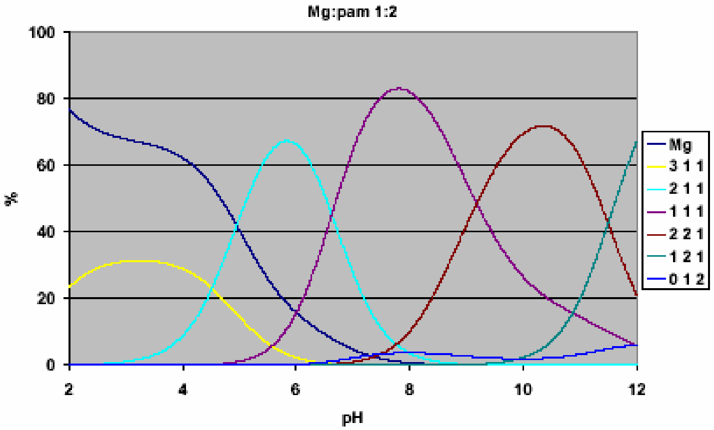
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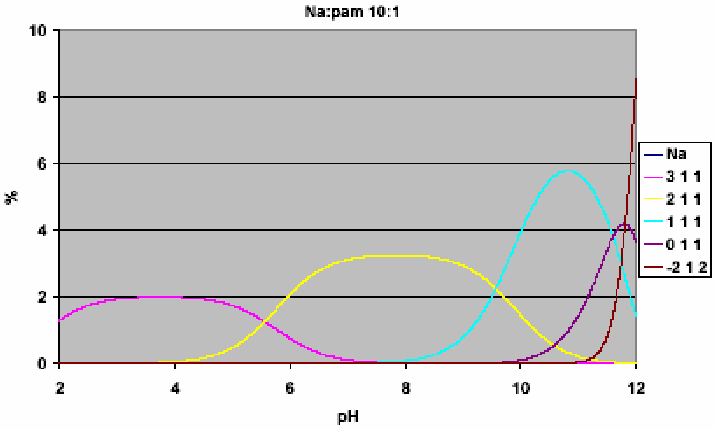
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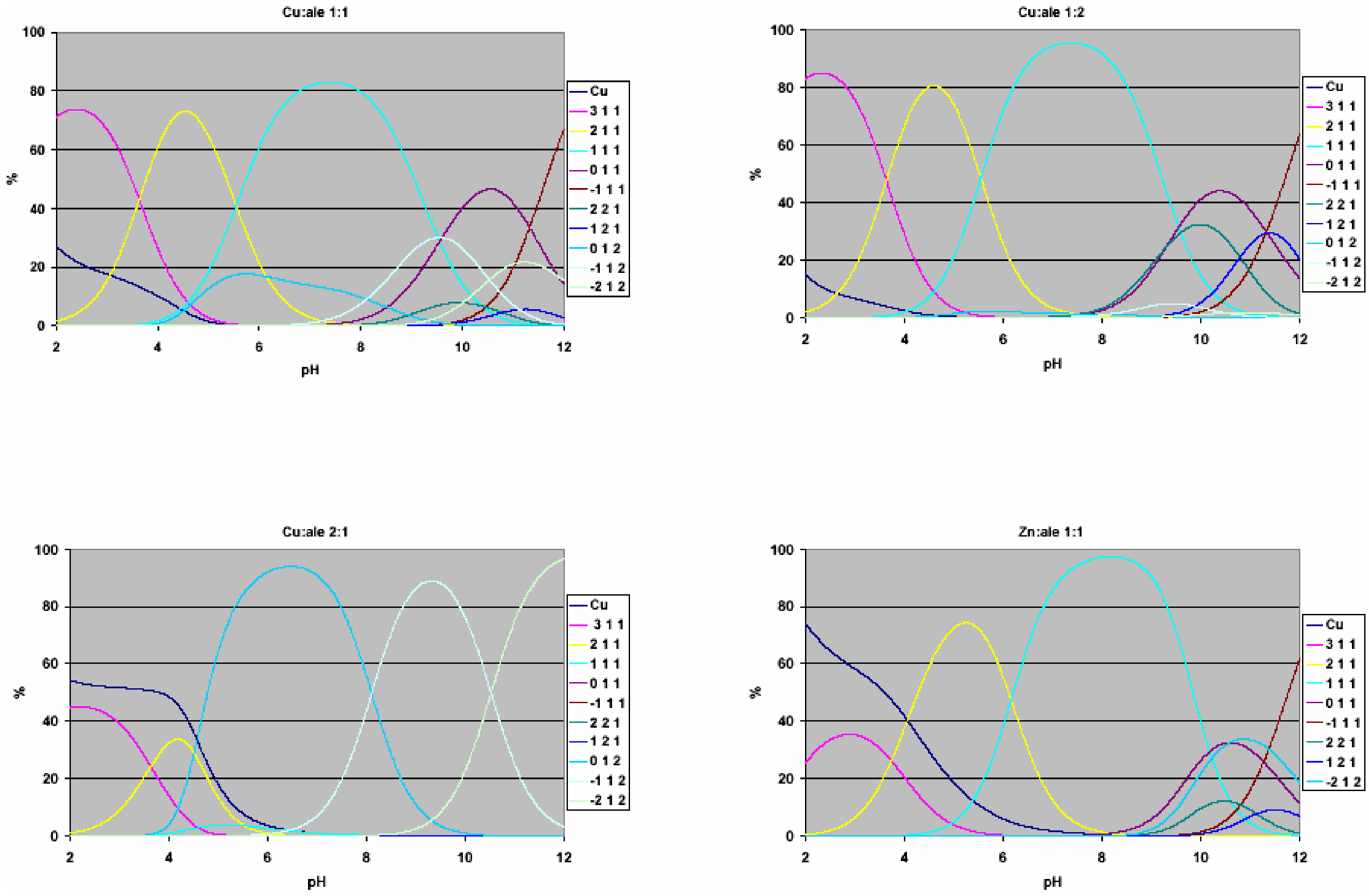
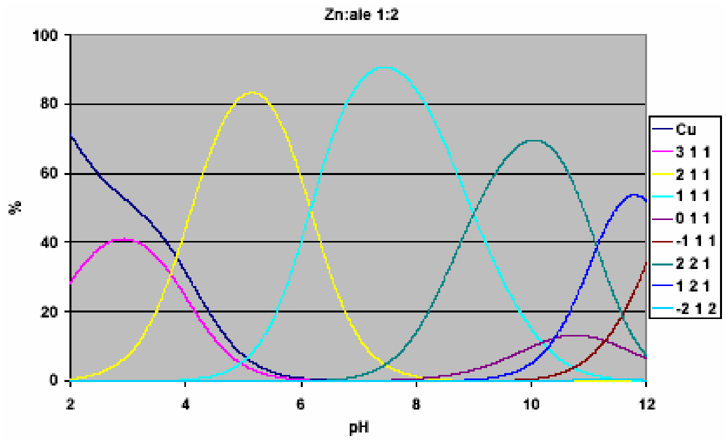
3 1 1
2 1 1
1 1 1
0 1 1
-2 1 2

Figure S4

Distribution diagrams of metal:H_4ale systems (abundance of the metal ions on the y axis, for pH region with precipitates see Table S1)

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40
20
0
%
2
4
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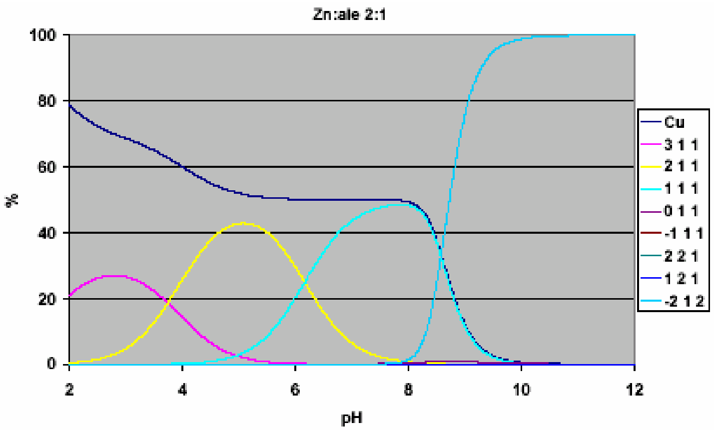
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Cu
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1 2 1
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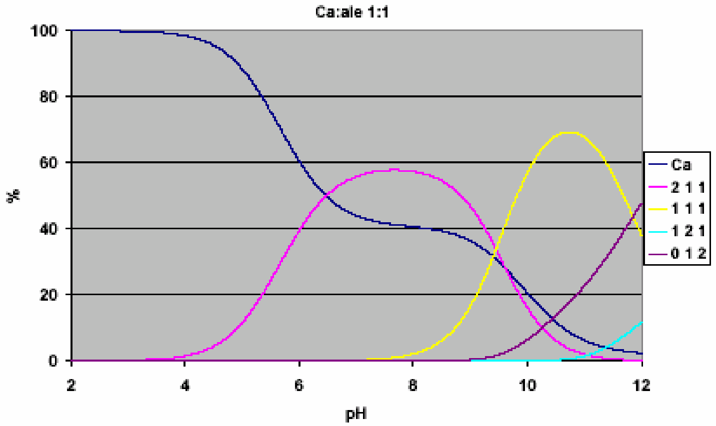
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%
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pH
Ca
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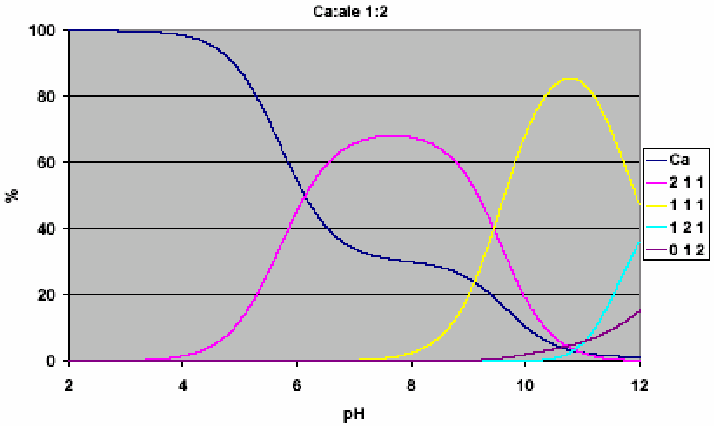
0 1 2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12
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Ca
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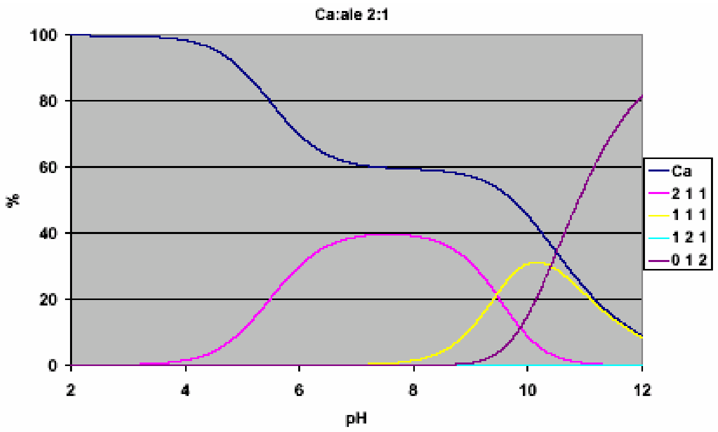
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Ca
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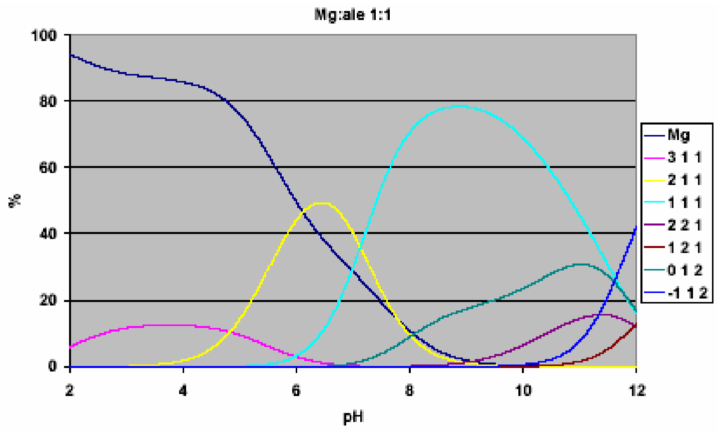
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pH
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60
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10
12
Mg
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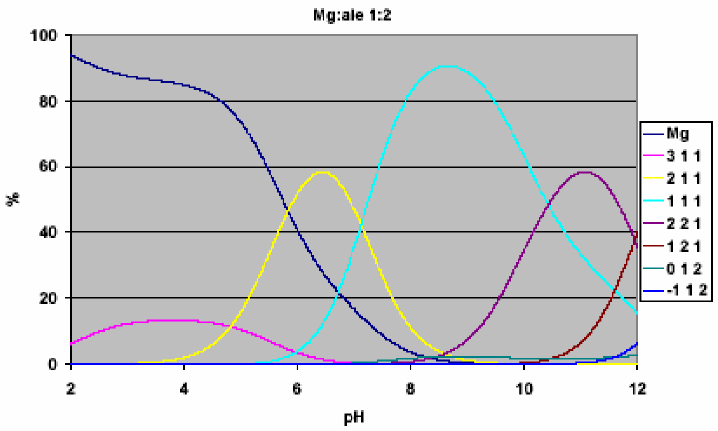
2 2 1
1 2 1
0 1 2
-1 1 2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pH
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6
8
10
12
Mg
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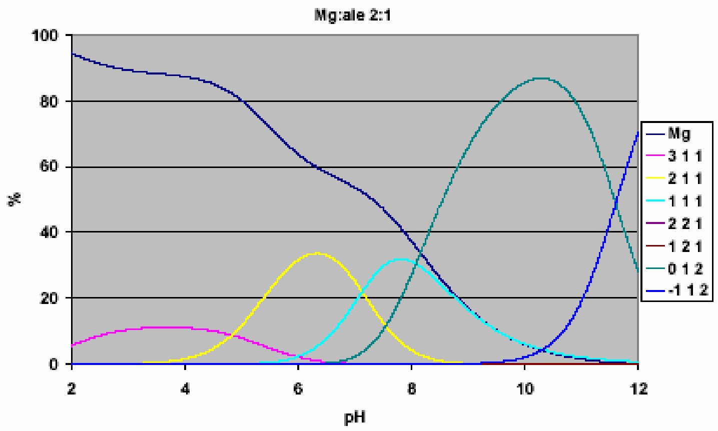
1 2 1
0 1 2
-1 1 2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%
pH
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80
60
40
20
0
2
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6
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10
12
Mg
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2 1 1
1 1 1
2 2 1
1 2 1
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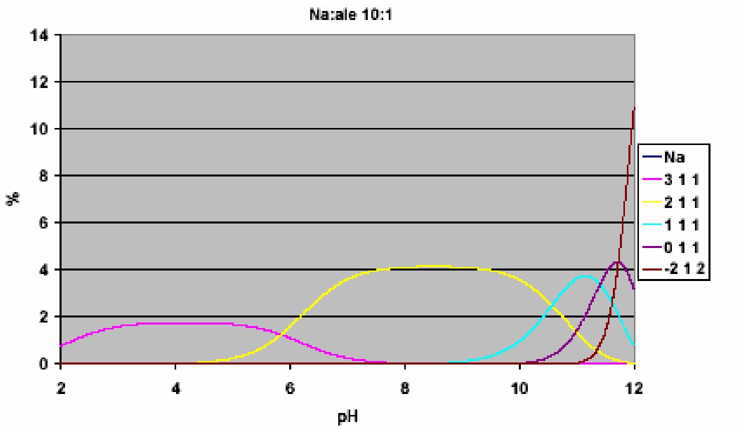
-1 1 2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6
4
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0
%
2
4
6
8
10
12
pH
Na
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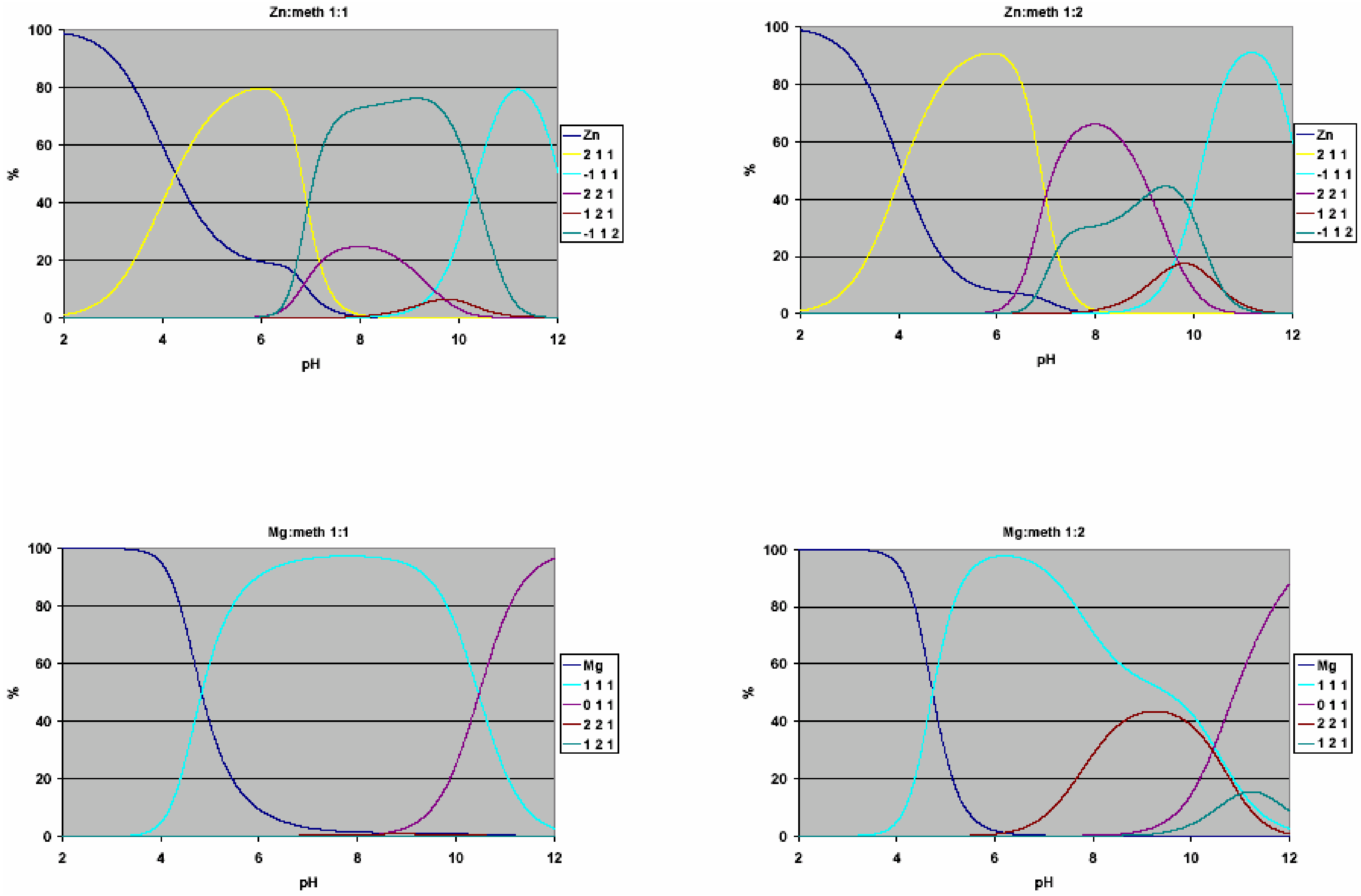
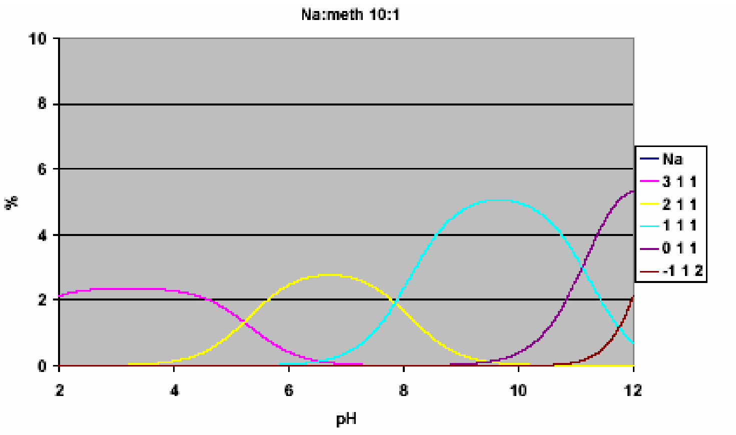
2 1 1
1 1 1
0 1 1
-2 1 2

Figure S5

Distribution diagrams of metal:H_4meth systems (abundance of the metal ions on the y axis, for pH region with precipitates see Table S1)

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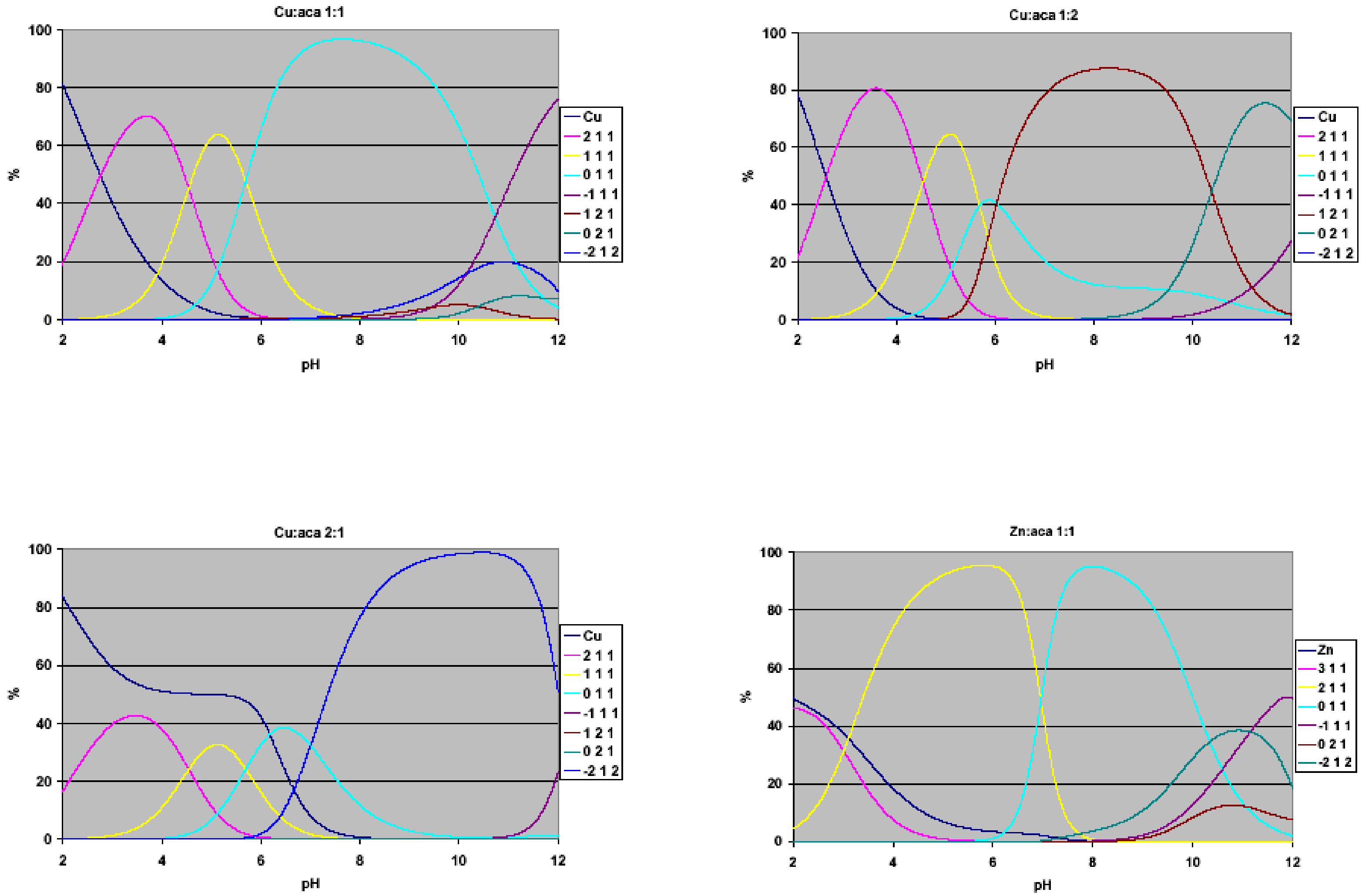
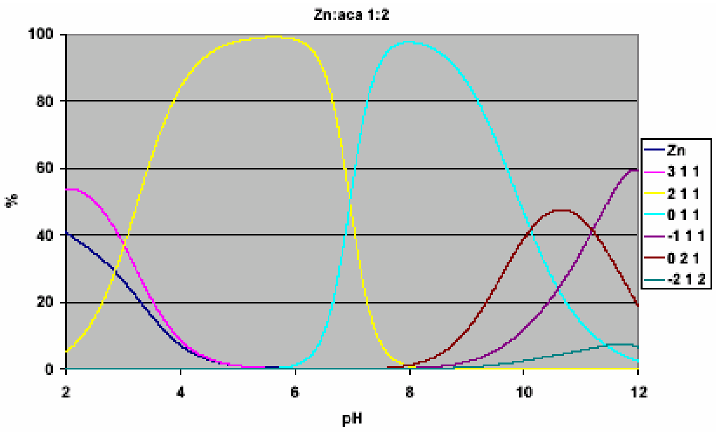
10
8
6
4
2
0
%
2
4
6
8
10
12
pH
Na
3 1 1
2 1 1
1 1 1
0 1 1
-1 1 2

Figure S6

Distribution diagrams of metal:H_4aca systems (abundance of the metal ions on the y axis, for pH region with precipitates see Table S1)

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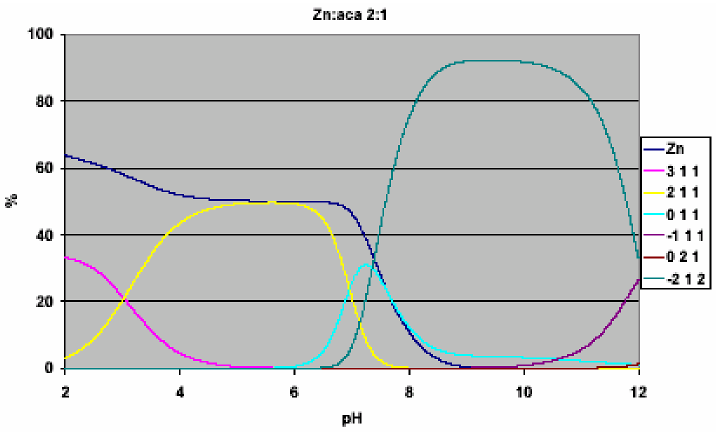
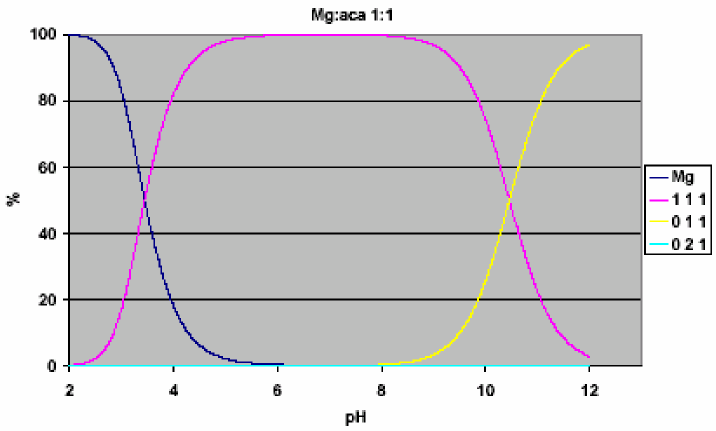
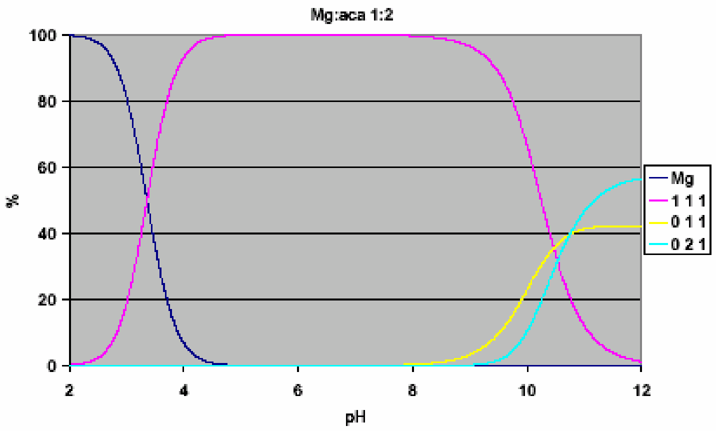
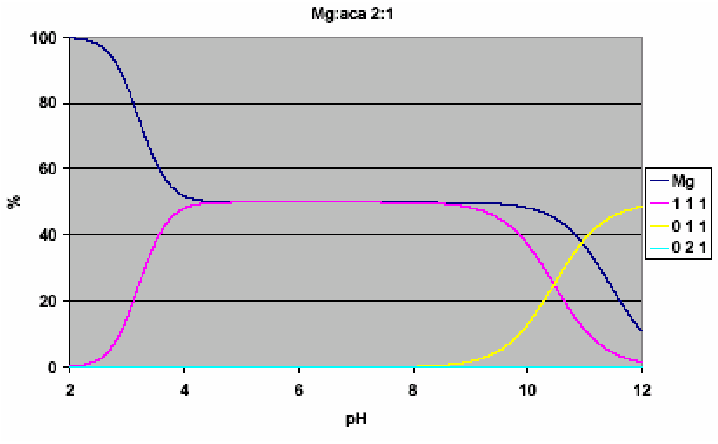

Zn:aca 2:1


Mg:aca 1:1


Mg:aca 1:2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100
80
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40
20
0
%
2
4
6
8
10
12
pH
Mg
1 1 1
0 1 1
0 2 1

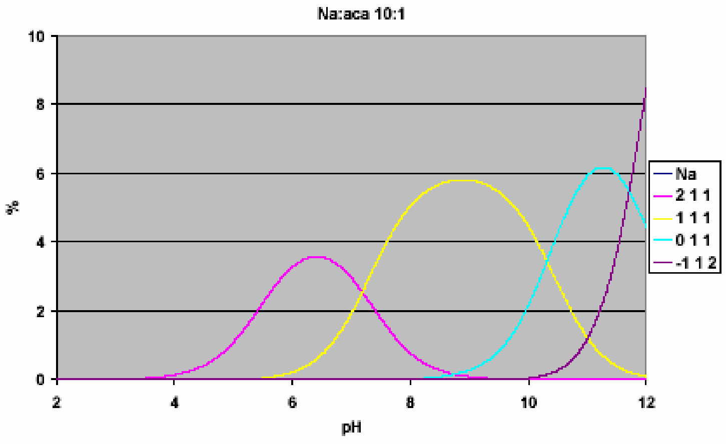
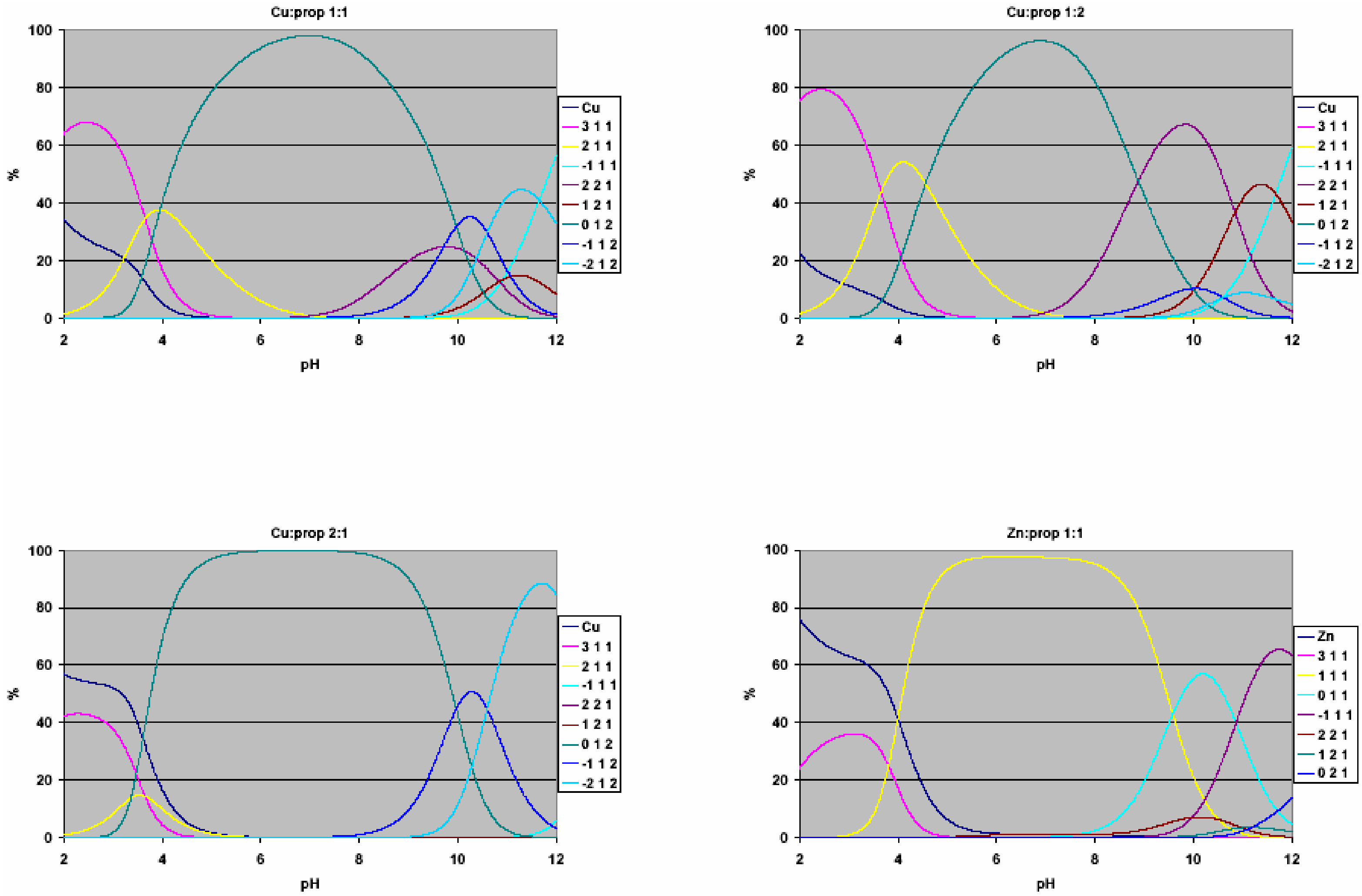
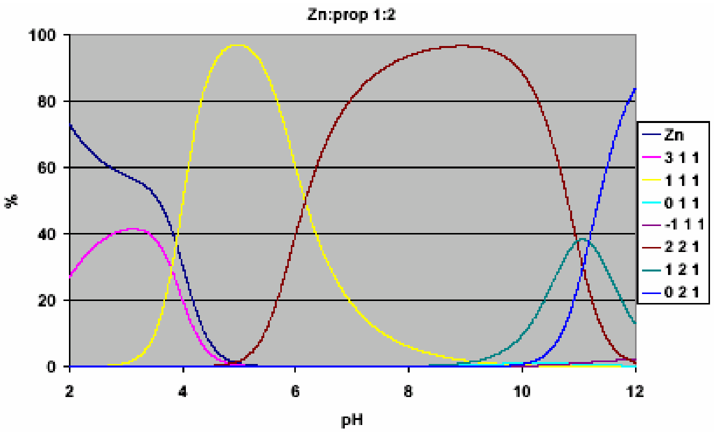
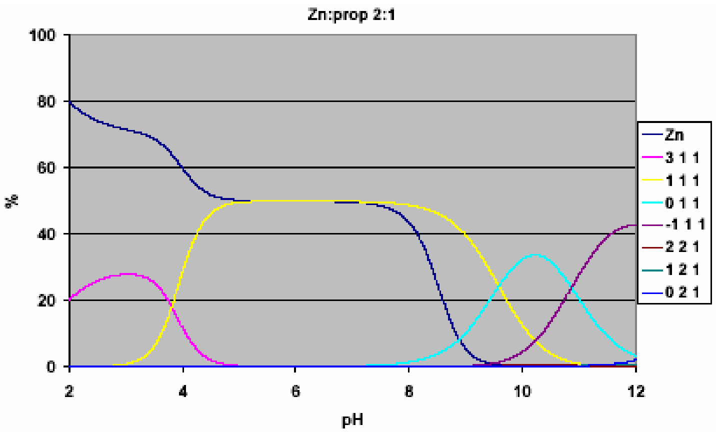

Na:aca 10:1
10
8
6
4
2
0
%
2
4
6
8
10
12
pH
Na
2 1 1
1 1 1
0 1 1
-1 1 2

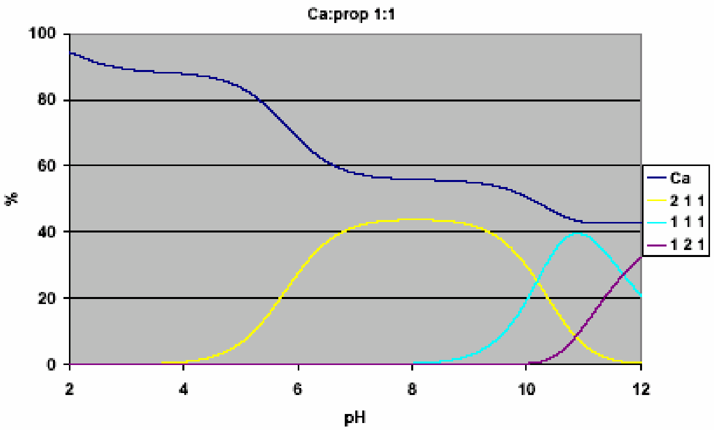
Figure S7

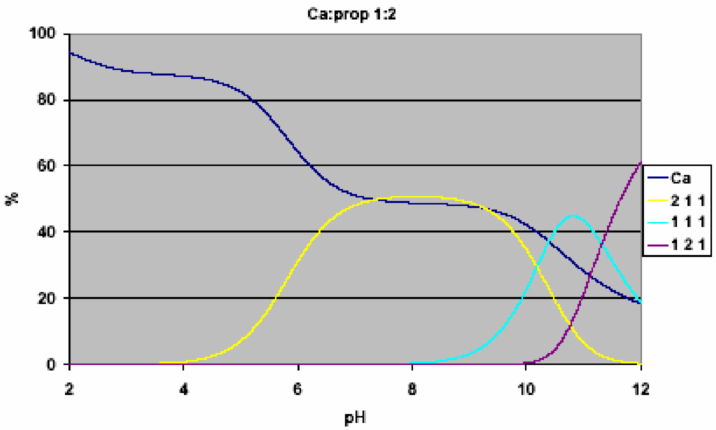
Distribution diagrams of metal:H_4prop systems (abundance of the metal ions on the y axis, for pH region with precipitates see Table S1)




Zn:prop 1:2


Zn:prop 2:1


Ca:prop 1:1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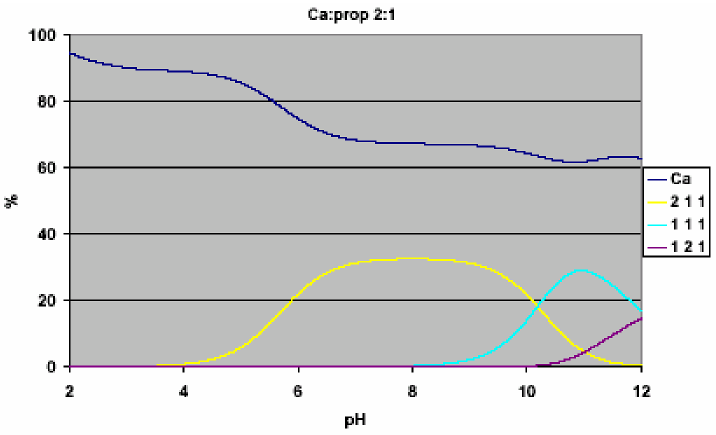
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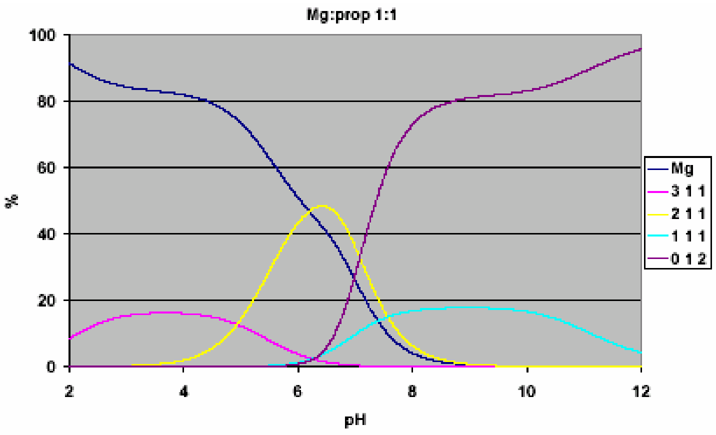
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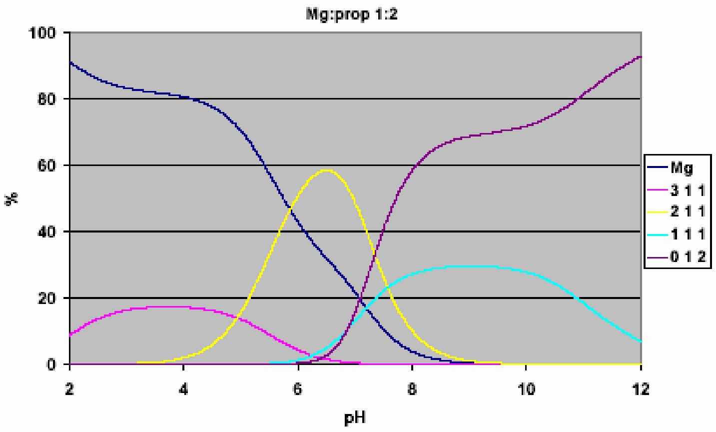
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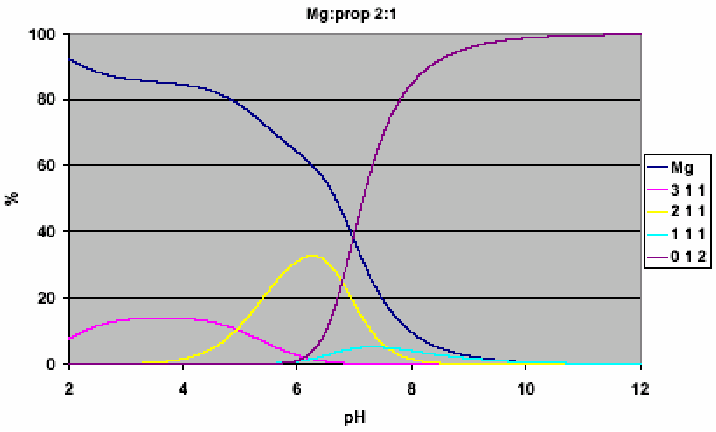
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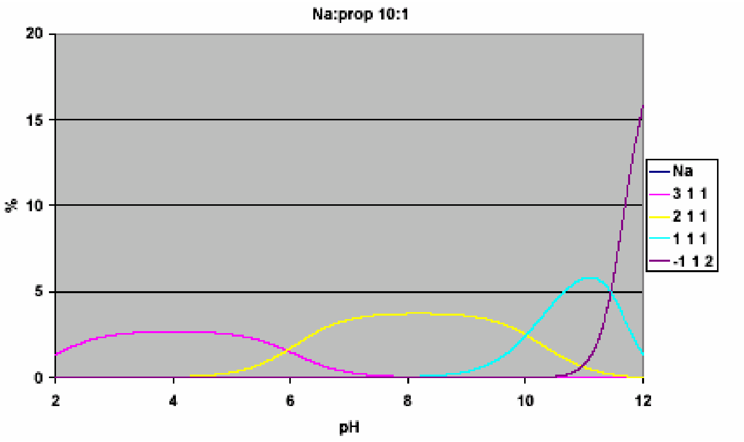
Na:prop 10:1
20
15
10
5
0
%
2
4
6
8
10
12
pH
Na
3 1 1
2 1 1
1 1 1
-1 1 2

Table S3

Hydrogen bonds in the structure of H_4aca·THF with H··A < *r*(A) + 2.000 Å and <DHA > 110º

D–H	*d*(D–H)	*d*(H··A)	<DHA	*d*(D··A)	A
N1–H11N	0.811	2.102	173	2.910	O13 [x-1, y, z]
O11–H11O	0.994	1.463	174	2.455	O23 [x+1, y, z]
O12–H12O	0.932	1.660	177	2.591	O13 [-x, -y+1, -z+2]
O21–H21O	0.998	1.500	171	2.490	O1A [-x, -y, -z+2]
O22–H22O	0.892	1.645	164	2.514	O1S

Table S4

Hydrogen bonds in the structure of $(NH_4)(H_3prop)\cdot H_2O$ with H··A < *r*(A) + 2.000 Å and <DHA > 110º

D–H	*d*(D–H)	*d*(H··A)	<DHA	*d*(D··A)	A
O11–H11O	0.932	1.644	171	2.569	O12 [-x+1/2, y-1/2, -z+1/2]
O21–H21O	0.753	1.958	166	2.693	O1W
N4–H41	0.926	2.027	171	2.946	O23 [x-1/2, y-1/2, z]
N4–H42	0.942	1.801	167	2.727	O22 [-x+1/2, -y-1/2, -z]
N4–H43	0.923	1.932	155	2.798	O12 [x, y-1, z]
N1A–H1A1	0.900	2.064	153	2.894	O13 [x+1/2, y+1/2, z]
N1A–H1A2	0.899	1.996	168	2.881	O23
N2A–H2A1	0.893	1.875	165	2.747	O13
N2A–H2A2	0.914	1.932	164	2.822	O23 [-x+1/2, y+1/2, -z+1/2]
O1W–H1W1	0.815	2.023	170	2.830	O22 [x, y+1, z]
O1W–H1W2	0.802	2.027	178	2.828	O13 [x+1/2, y+1/2, z]

Table S5

Hydrogen bonds in the structure of $(NH_4)_3Hmeth\cdot H_2O$ with H··A < *r*(A) + 2.000 Å and <DHA > 110º

D–H	*d*(D–H)	*d*(H··A)	<DHA	*d*(D··A)	A
N1–H1N1	0.842	2.161	150	2.922	O1W [-x+1/2, y-1/2, z-1/2]
N1–H1N1	0.842	2.621	112	3.036	O12
N1–H1N2	0.934	1.772	174	2.702	O21 [-x, -y, z+1/2]
N1–H1N3	0.886	1.962	157	2.801	O23 [-x, -y, z-1/2]

O1W–H1W1	0.847	2.065	167	2.895	O12
O1W–H1W2	0.870	1.910	170	2.771	O13 [x, y, z+1]
N1A–H1A1	0.847	2.045	164	2.868	O13 [x, y, z+1]
N1A–H1A2	0.897	1.841	170	2.729	O11
N1A–H1A3	0.827	2.041	177	2.867	O22 [-x, -y+1, z+1/2]
N1A–H1A4	0.955	1.863	176	2.817	O12 [-x+1/2, y+1/2, z+1/2]
N2A–N2A1	0.862	1.898	177	2.760	O13 [x, y, z+1]
N2A–N2A2	0.873	1.968	168	2.829	O12
N2A–N2A3	0.849	1.980	172	2.824	O11 [-x+1/2, y-1/2, z+1/2]
N2A–N2A4	0.933	1.787	160	2.683	O23 [-x, -y, z+1/2]
N3A–H3A1	0.803	1.993	177	2.795	O22 [-x, -y+1, z-1/2]
N3A–H3A2	0.836	2.194	153	2.963	O1W [-x+1/2, y+1/2, z-1/2]
N3A–H3A3	0.922	1.957	149	2.789	O22
N3A–H3A3	0.922	2.462	119	3.014	O11
N3A–H3A4	0.875	1.836	167	2.697	O21 [-x, -y+1, z+1/2]

Table S6

Hydrogen bonds in the structure of $\{[Cu_2(H_2pam)_2]\cdot H_2O\}_n$ with H··A < *r*(A) + 2.000 Å and <DHA > 110º

D–H	*d*(D–H)	*d*(H··A)	<DHA	*d*(D··A)	A
O12–H12O	1.036	1.387	178	2.423	O22 [-x+2, y+1/2, -z+1/2]
O1C–H1C	0.863	1.856	169	2.708	O11 [x+1, y, z]
N4–H41	0.777	2.082	149	2.777	O1W
N4–H42	0.895	2.196	160	3.052	O1C [-x+2, -y+1, -z]
N4–H43	0.856	2.070	162	2.897	O21 [x, -y+1/2, z-1/2]
O1W–H1W1	0.814	2.248	139	2.912	O13 [-x+2, y-1/2, -z+1/2]
O1W–H1W2	0.769	2.094	170	2.855	O22 [x-1, y, z]