Table S1 Hydrolysis formation constants of Zn^{2+} and Cu^{2} in NaCl

		logβ [a)]				
Species	M	$I = 0.15$ [b)] $T = 298.15$ K	$I = 0.5$ [b)] $T = 298.15$ K	$I = 1$ [b)] $T = 298.15$ K	$I = 0.15$ [b)] $T = 288.15$ K	$I = 0.15$ [b)] $T = 305.15$ K
MOH^{+}	Zn^{2+} [c)]	-9.14	-9.07	-8.88	-10.48	-8.38
$M(OH)_2^{0}$		-17.1	-17.1	-16.9	—	-14.8
$M(OH)_3^{-}$		-28.4	-28.35	-28.3	—	—
$M(OH)_4^{2-}$		-40.8	-40.4	-40.2	-41.5	-41.5
M_2OH^{3+}		-8.7	-9.3	-9.9	—	—
$M_2(OH)_6^{2-}$		-57.5	-57.3	-57.1	—	—
MOH^{+}	Cu^{2+} [d)]	-7.6	-7.6	-7.5	-7.9	-7.5
M_2OH^{3+}		-6.10	-6.07	-6.11	-6.40	-5.88
$M_2(OH)_2^{2+}$		-10.72	-10.79	-10.77	-11.13	-10.36
$M_3(OH)_4^{2+}$		-21.36	-22.64	-23.95	-22.43	-20.70

[a)] Refer to the reaction: $pM^{2+} + qH_2O = M_p(OH)_q^{(2p-q)} + qH^{+}$; [b)] Expressed in mol L^{-1}; [c)] Baes, C. F.; Mesmer, R. E., *The hydrolysis of cations*. John Wiley & sons: New York, 1976; Pettit, L. D.; Powell, K. J. *IUPAC Stability Constants Database.*, Academic Software, IUPAC: 2001. [d)] MOH, M_2OH, $M_2(OH)_2$ data: (De Robertis, A.; De Stefano, C.; Foti, C.; Signorino, G., Thermodynamic Parameters for the formation of Dimeric Hydrolytic Species of Copper(II) in Aqueous $NaClO_4$ Solution at Different Ionic Strengths. *Talanta* **1997,** 44, 1839-1846; $Cu_3(OH)_4$ data: Rigano, C.; De Robertis, A.; Sammartano, S., Computer Analysis of Equilibrium Data in Solution. A Method for Computing the Formation Constants of two Mass Balance Systems, from Potentiometric Measurements, Applied to the Hydrolysis of Copper(II). *Transition Met. Chem.* **1985,** 10, 1-4.

Table S2 Protonation constants of AsO_4^{3-} at different temperatures and ionic strengths in NaCl

I / mol L^{-1}	T / K	$\log\beta_1$ [a) b)]	$\log\beta_2$ [a) b)]	$\log\beta_3$ [a) b)]
0.15	298.15	11.03	17.64	19.86
0.5	298.15	10.62	17.00	19.08
1	298.15	10.51	16.78	18.81
0.15	288.15	11.14	17.81	20.04
0.15	310.15	10.91	17.49	19.66

[a)] Refer to the reaction: $pH^+ + AsO_4^{3-} = H_pAsO_4^{(3-p)-}$
[b)] Chillè, D., Foti, C., Giuffrè, O., 2018. Thermodynamic parameters for the protonation and the interaction of arsenate with Mg^{2+}, Ca^{2+} and Sr^{2+}: Application to natural waters. Chemosphere 190, 72-79; Cassone, G., Chillè, D., Foti, C., Giuffrè, O., Ponterio, R.C., Sponer, J., Saija, F., 2018. Stability of hydrolytic arsenic species in aqueous solutions: As^{3+} vs. As^{5+}. Phys. Chem. Chem. Phys. 20, 23272-23280.

Table S3 Calculation trials on Cu^{2+}-AsO_4^{3-} (L) system at T = 298.15 K and I = 0.15 mol L^{-1} in NaCl

Species	logβ [a)]			
MLH_2	—	—	—	20.85(7) [b)]
MLH	—	—	13.6(2) [b)]	15.47(8)
ML	9.86(1) [b)]	9.99(1) [b)]	9.99(1)	10.71(5)
MLOH	—	1.85(3)	1.84(3)	2.73(6)
	σ^2/σ_0^2 = 1.91 [c)]	σ^2/σ_0^2 = 1.15 [c)]	σ^2/σ_0^2 = 1.13 [c)]	σ^2/σ_0^2 = 1.00 [c)]

[a)] Refer to the reaction M + L + rH = MLH_r, charges omitted for simplicity; [b)] 95% confidence interval; [c)] variance ratio, σ^2/σ_0^2 (σ_0^2 = variance for the best fit, σ^2 = variance of the fit).

Table S4 Experimental formation constant values of Cu^{2+}(M)-AsO_4^{3-}(L) species obtained by spectrophotometry at I = 0.15 mol L^{-1} in NaCl and T = 298.15 K

Species	logβ [a)]
MLH_2	21.44
MLH	15.88
ML	10.83(4) [b)]
MLOH	2.40

[a)] According to the reaction M + L + rH = MLH_r; [b)] least-squares errors on the last significant figure are given in parentheses.

Table S5 Maximum values of molar extinction coefficients and wavelengths corresponding to the individual Cu^{2+}(M), hydrolytic and Cu^{2+}(M)-AsO_4^{3-}(L) complex species, at T = 298.15 K and I = 0.15 mol L^{-1} in NaCl

Species	ε_{max} / L mol^{-1} cm^{-1}	λ / nm
M	2 828(51)[a)]	207
$M_2(OH)_2$	6 099(100)	206
ML	3 490(73)	207

[a)] Least-squares errors on the last significant figure are given in parentheses..

Table S6 Mass spectrometry data of Cu^{2+}(M)-AsO_4^{3-}(L) species, reported as m/z values, formulae assignments, MS/MS values for fragment ions

		m/z	Δppm
$[MLH_2]^+$	**$[CuH_2AsO_4]^+$**	**203.85**	**5**
MS/MS	$[CuH_2AsO_3]^+$	187.85	13
	$[CuAsO_3]^+$	185.84	11
	$[CuH_3AsO_2]^+$	172.87	12
	$[AsH_4O_4]^+$	142.93	15
	$[AsH_2O_2]^+$	108.93	13
	$[CuOH]^+$	79.93	12
	$[Cu]^+$	62.93	10

Table S7 Mass spectrometry data of Zn^{2+}(M)-AsO_4^{3-}(L) species, reported as m/z values, formulae assignments, MS/MS values for fragment ions

		m/z	Δppm
$[MLH_2]^+$	**$[ZnH_2AsO_4]^+$**	**204.85**	**5**
MS/MS	$[ZnH_2AsO_3]^+$	188.85	17
	$[ZnAsO_3]^+$	186.84	12
	$[ZnAsO_2]^+$	170.84	10
	$[AsH_4O_4]$+	142.93	17
	$[AsH_2O_2]^+$	108.93	11
	$[ZnH_3O_2]^+$	98.94	12
	$[ZnOH]^+$	80.93	11
	$[Zn]^+$	63.93	10
$[ML_2H_5]^+$	**$[ZnH_5As_2O_8]^+$**	**344.77**	**5**
MS/MS	$[ZnH_3As_2O_7]^+$	328.76	9
	$[ZnH_2AsO_4]$+	204.85	5
	$[ZnAsO_3]^+$	186.84	12
	$[ZnOH]^+$	80.93	11

Table S8 Recalculated formation constant values of Cu^{2+}-AsO_4^{3-}(L) and Zn^{2+}-AsO_4^{3-}(L) species

	logβ [a]				
Species	I = 0.0016 [b]	I = 0.15 [b]	I = 0.5 [b]	I = 0.7 [b]	I = 1 [b]
$CuLH_2$	22.38(9)	20.91(9)	20.25(8)	20.07(9)	19.89(9)
CuLH	17.03(7)	15.50(5)	14.71(8)	14.45(9)	14.16(9)
CuL	12.06(9)	10.73(8)	9.98(5)	9.73(5)	9.42(8)
CuLOH	3.69(7)	2.70(6)	1.96(3)	1.65(3)	1.25(6)
ZnL	9.02(4)	7.65(9)	6.81(8)	6.50(6)	6.12(6)
ZnL_2	11.99(5)	11.35(4)	11.02(3)	10.93(3)	10.82(5)

[a] Referred to the reaction M + L + rH = MLH_r; [b] expressed in mol L^{-1}.

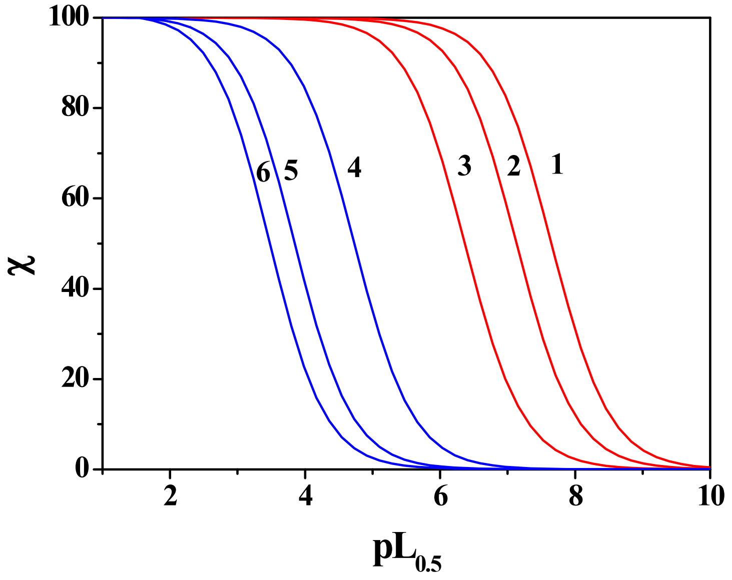

Fig. S1 Sum of the species fractions for Cu^{2+}-AsO_4^{3-} (in red) and Zn^{2+}-AsO_4^{3-} (in blue) systems at I = 0.15 mol L^{-1} (**1, 4**), I = 0.5 mol L^{-1} (**2, 5**), I = 1 mol L^{-1} (**3, 6**) in NaCl, at pH = 8.1 and T = 298.15 K.

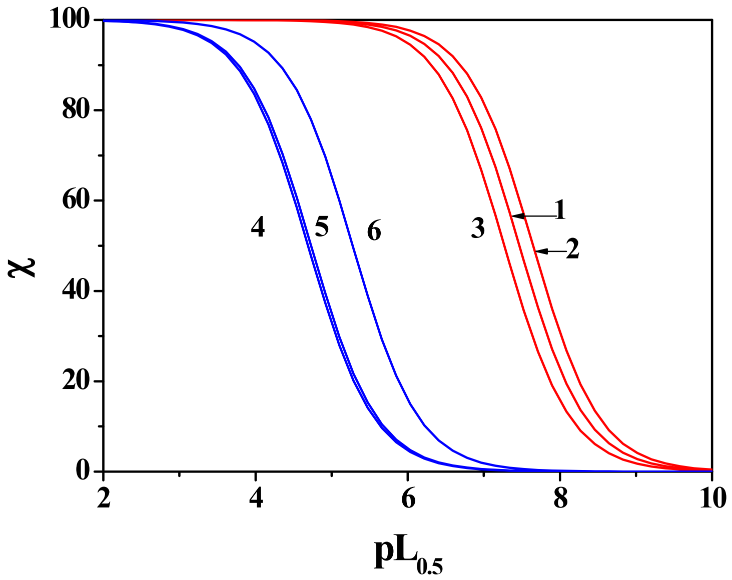

Fig. S2 Sum of the species fractions for Cu^{2+}-AsO_4^{3-} (in red) and Zn^{2+}-AsO_4^{3-} (in blue) systems at I = 0.15 mol L^{-1} in NaCl, pH = 8.1, T = 288.15 K (**1, 4**), T = 298.15 K (**2, 5**), T = 310.15 K (**3, 6**).

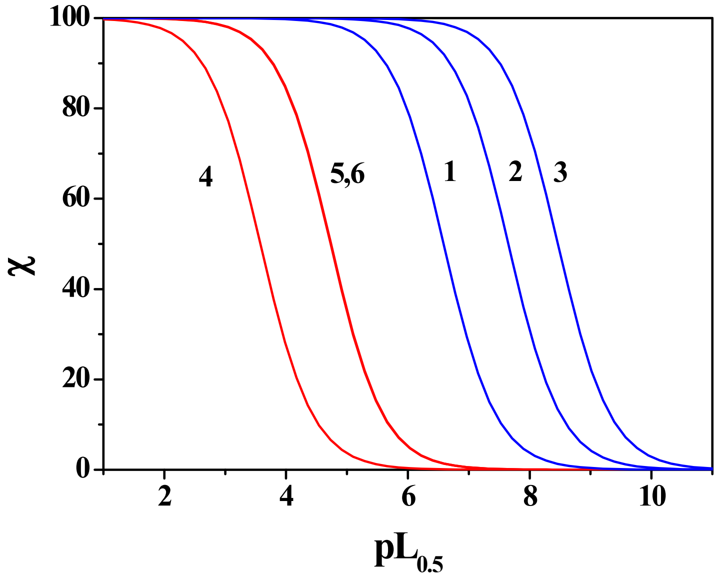

Fig. S3 Sum of the species fractions for Cu^{2+}-AsO_4^{3-} (in red) and Zn^{2+}-AsO_4^{3-} (in blue) systems at pH = 7.0 (**1, 4**), pH = 8.1 (**2, 5**), pH = 9.0 (**3, 6**), at I = 0.15 mol L^{-1} in NaCl, T = 298.15 K.