Evaluation of the Activity Coefficients of some Sulfonated Azo Dyes and of their Complexes with Metal Ions

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The protonation and complexation conditional constants of equilibria involving large, multicharged organic ions depend on the ionic medium in which they occur. The possibility of evaluating these effects on the basis of the Specific Interaction Theory (SIT) was tested, by determining spectrophotometrically the conditional protonation constants (in concentration) of some bisulfonated azo dyes [2-hydroxy-1-(1*H*-tetrazol-5-ylazo)naphthalene-3,6-disulfonic acid, 1,8-dihydroxy-2-(1*H*-tetrazol-5-ylazo)naphthalene-3,6-disulfonic acid and 1,8-dihydroxy-2-(*p*-nitrophenylazo)-naphthalene-3,6-disulfonic acid] at different sodium perchlorate concentrations. The same was done for complexation with thorium(IV), indium(III) and copper(II). It was found that the dependance of protonation and complexation conditional constants on the ionic medium can be described by evaluating the activity coefficients of the ions on the basis of SIT. The activity coefficients of the multicharged free organic ligands are best estimated by considering their charge globally, exactly like in the case of small inorganic ions. On the other hand, the activity coefficients of the complexes with a metal ion are best evaluated by considering them as bearing two separate charged sites, one corresponding to the site where the metal ion is bound, and the other to the residual charge of the ligand. In this way the specific interaction coefficients were found to be constant, as expected from SIT, and their summations were experimentally determined, together with the thermodynamic constants, by linear extrapolation.

Protonation and complex formation properties of organic reagents have been widely investigated. Usually they are studied in solutions with a well defined ionic strength, obtained by adding an inert salt at high concentration, according to the constant ionic medium method.[1] In this way conditional protonation and complexation constants are obtained, holding only in the considered ionic medium, while in practical applications the solution composition can vary over wide ranges. Hence it is important to be able to convert the conditional constant obtained in a particular ionic medium into that holding in a different one. This can be done by evaluating the activity coefficients of the species involved in the considered media [see eqns. (4) and (5)]. In the case of small inorganic ions, the Specific Interaction Theory (SIT), proposed by Brönsted,[2] Scatchard[3] and Guggenheim,[4] and more recently by Biedermann[5] can be conveniently applied.

SIT states that the activity coefficient γ_i of an ion i with charge z_i is given by eqn. (1) at 25 °C. The first term to the

$$\log \gamma_i = -z_i^2\, 0.51\, I^{\frac{1}{2}}/(1 + 1.5\, I^{\frac{1}{2}}) + \Sigma b(\mathrm{i,j})\, m_j \qquad (1)$$

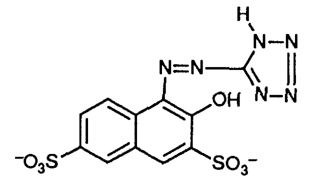
right is equal to that of the Debye–Hückel equation, in which $\mathring{a}B = 1.5$. The summation of the second term extends to all the ions in solution at a concentration m_j (mol kg^{-1}), b(i,j) indicates the specific interaction coefficients which, according to the Brönsted hypothesis, are assumed to be different from zero only for ions j with charge sign opposite to that of i. b(i,j) can be evaluated from the mean activity coefficient of the electrolyte ij in its own solution at ionic strength I. It is important to underline that b(i,j) is independent of the ionic strength of the solution I up to $I = 3.5$ mol kg^{-1}, as Guggenheim[4] demonstrated for monocharged inorganic ions.

While eqn. (1) has been widely used in the case of equilibria involving small inorganic ions, only recently has it been tested in the case of large, multicharged organic ions, by Salvatore *et al.*[6,7] They found that the conditional protonation constants of organic reagents depended on the ionic composition of the solution according to SIT, but in some cases the charges had to be considered as distributed globally over the molecule,[7] while in other cases as if they were isolated.[6] This point was first discussed by Bjerrum[8] and Kolthoff,[9] who pointed out that the electrical work required to charge an ion with *n* isolated charges is equal to that required to charge *n* univalent ions.

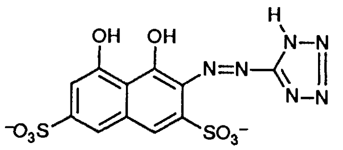
Some preliminary observations on the complexation equilibria of the sulfonated azo dyes, studied in our laboratory, showed that sometimes the charge of the complex ion was not to be considered globally, but as distributed on separate sites. This was particularly evident when metal ions with high charge were considered. No information on this point could be found in the literature.

In this context three sulfonated azo dyes were considered. Two of them had a heterocyclic ring in the diazo moiety, and were synthesized for their good complexing ability towards heavy metal ions: 2-hydroxy-1-(1*H*-tetrazol-5-ylazo)naphthalene-3,6-disulphonic acid (T-azo-R),[10] and 1,8-dihydroxy-2-(1*H*-tetrazol-5-ylazo)naphthalene-3,6-disulphonic acid (T-azo-C).[11] The third dye was a disulfonated azo dye which is available on the market: 2-1,8-dihydroxy-(*p*-nitrophenylazo)-naphthalene-3,6-disulfonic acid (Chromotrope 2B). They bear the following charges, depending on their state of protonation: T-azo-R (H_2L^{2-}, HL^{3-}, L^{4-}), T-azo-C (H_3L^{2-}, H_2L^{3-}, HL^{4-}), Chromotrope 2B (H_2L^{2-}, HL^{3-}). In the following text, charges will be omitted for simplicity.

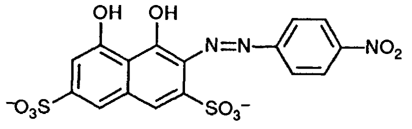
The influence of increasing concentrations of sodium perchlorate on their protonation and complexation equilibria was investigated. The effect of ionic strength on the complexation equilibria involving large organic ions has been much less investigated than the protonation equilibria. Therefore this point was considered with particular attention in this study. Three metal ions were chosen for the investigation, on the basis of their charge, and the stoichiometry of their complexes with the azo dyes: thorium(IV), indium(III) and copper(II).



T-azo-R



T-azo-C



Chromotrope 2B

Sodium perchlorate was used as the ionic medium in order to negate any complexation of metal ions by the ionic medium itself.

Experimental

Reagents.—Azo-dyes. Chromotrope 2B was obtained from C. Erba (RPE: Pure Reagent Erba), and was used without further purification. T-azo-R and T-azo-C were synthesized and purified as previously described.[10,11] Standard solutions were prepared by weighing of the solid substances.

Buffers. Up to pH = 3.5, a measured amount of standard perchloric acid was added to the solution, and the value of pH = −log [H] obtained was checked potentiometrically in a cell standardized in proton concentration as described below. The determinations at pH 8.66 were made in a buffer ammonia/ammonium perchlorate (0.010 mol kg^{-1} $HClO_4$, 0.012 mol kg^{-1} NH_4OH), whose pH (proton concentration) was measured potentiometrically. In order to minimize the variations of the protonation constant of ammonia with ionic strength, only sodium perchlorate concentrations lower than 0.3 mol kg^{-1} were considered in this study.

Other reagents. These were of analytical grade, and water was triply distilled.

Apparatus.—A Varian DMS 100 spectrophotometer and an Orion 701 A digital ionalyser pH meter, equipped with a combined Ross-type glass electrode (Orion 8102-SC), were used. The potentiometric cell was standardized in H^+ concentration, by adding standard perchloric acid to a solution of the same ionic strength as that measured, and by treating the data (measured potential) − (amount of H^+ added) by Gran's method.[11]

Method and Calculations.—The protonation and complexation equilibria at fixed ionic strength were studied with the spectrophotometric method previously described.[10,11]

Dependence of the protonation equilibria on the ionic medium concentration. The absorbance (A) (at fixed wavelength) of solutions with constant c_L and pH was investigated at increasing concentrations of sodium perchlorate. The protonation reaction and its conditional equilibrium constant are given by eqn. (2). The concentrations of H_xL and $H_{x-1}L$ were calculated from the absorbance measured at a fixed wavelength, where the molar absorbances ε (dm^3 cm^{-1} mol^{-1}) of the species are known. The following relationships were considered:

$$H_{x-1}L + H \longleftrightarrow H_xL \quad K_x = \frac{[H_xL]}{[H_{x-1}L][H]} = K_{T_x}\frac{\gamma_{H_{x-1}L}\gamma_H}{\gamma_{H_xL}} \qquad (2)$$

$$A = \varepsilon_{H_xL}[H_xL] + \varepsilon_{H_{x-1}L}[H_{x-1}L]$$
$$c_L = [H_xL] + [H_{x-1}L]$$

By evaluating the activity coefficients of the ionic species with eqn. (1), expression (3) was obtained for the dependance of log K_x on I. Y and N represent, respectively, the anion and the cation of the medium salt. Eqn. (3) holds when the ionic medium is pure NY. In the experiments made here the ionic medium was mixed, (Na,H)ClO_4 or (NH_4,H)ClO_4. However, at ionic strengths higher than 0.1 mol kg^{-1}, at which the specific interaction term became important, the concentration of cations other than sodium was low compared with that of sodium. Thus the interaction terms bm_j pertinent to different cations could be neglected.

K_{T_x} is the thermodynamic protonation constant, given by eqn. (4). The parameter $Z = z_H{}^2 + z_{H_{x-1}L}{}^2 - z_{H_xL}{}^2$ was

$$K_{T_x} = \frac{a_{H_xL}}{a_{H_{x-1}L}a_H} = K_x\frac{\gamma_{H_xL}}{\gamma_{H_{x-1}L}\,\gamma_H} \qquad (4)$$

determined at ionic strength lower than 0.2 mol kg^{-1}, where the term containing the specific interaction coefficients can be neglected. By plotting log K_x *vs.* $0.51\,I^{\frac{1}{2}}/(1 + 1.5\,I^{\frac{1}{2}})$ a straight line with slope Z was obtained. The other parameters, log K_{T_x} and $S = b(H,Y) + b(H_{x-1}L,N) + b(H_xL,N)$, were obtained by plotting log $K_x + Z\,0.51\,I^{\frac{1}{2}}/(1 + 1.5\,I^{\frac{1}{2}})$ *vs.* I.

The variation of water activity was neglected, since it is of only 0.01 log units on passing from 0 to 1 mol kg^{-1} sodium perchlorate.

Dependence of the Complexation equilibria on the ionic medium concentration. This was examined by a procedure similar to that described above for the protonation equilibria. Let's consider the following equilibrium (5). K_c can be evaluated by means

$$mM + pH_xL \longleftrightarrow M_mH_rL_p + qH$$
$$K_c = \frac{[M_mH_rL_p][H]^q}{[M]^m[H_xL)]^p} = K_{Tc}\frac{\gamma_M{}^m\,\gamma_{H_xL}{}^p}{\gamma_{MmHrL_p}\,\gamma_H{}^q} \qquad (5)$$

of the following equations, which hold when $c_M \gg c_L$.

$$A = \varepsilon_{H_xL}[H_xL] + \varepsilon_{H_{x-1}L}[H_{x-1}L] + \varepsilon_{M_mH_rL_p}[M_mH_rL_p]$$
$$c_M = [M]$$
$$c_L = [H_xL] + [H_{x-1}L] + [M_mH_rL_p]$$

K_{Tc} is the thermodynamic complexation constant, given by eqn. (6).

$$K_{Tc} = \frac{a_{M_mH_rL_p}\,a_H{}^q}{a_M{}^m\,a_{H_xL}{}^p} \qquad (6)$$

By evaluating the activity coefficients with eqn. (1), the conditional complexation constant depends on the ionic strength according to relationship (7),
where

$$\alpha_{H_xL} = \frac{\Sigma\beta_i[H]^i}{\beta_x[H]^x}\quad \varepsilon_{H_xL}{}' = \frac{\Sigma\varepsilon_{H_iL}\beta_i[H]^i}{\beta_x[H]^x}$$

with $\beta_i = K_1K_2\ldots K_i$ and $\beta_0 = 1$. The summations are extended from 0 to x.

$$\log K_x = \log\frac{(\varepsilon_{H_{x-1}L}\,c_L - A)}{(A - \varepsilon_{H_xL}c_L)} + \mathrm{pH} = \log K_{T_x} - \frac{0.51\,I^{\frac{1}{2}}}{1 + 1.5\,I^{\frac{1}{2}}}(z_{H_{x-1}L}{}^2 + z_H{}^2 - z_{H_xL}{}^2) + [b(H_{x-1}L,N) + b(H,Y) - b(H_xL,N)]I \qquad (3)$$

Table 1 Effect of increasing concentrations of $NaClO_4$ on the first protonation of the disulfonated azo-dyes T-azo-R,[a] T-azo-C[b] and Chromotrope 2B.[c] The ionic medium is $(NH_4,Na)ClO_4$. I is in mol kg^{-1}.

T-azo-R				T-azo-C			
I	A_{490}	$\log K_1$	$\log K_{1(est)}$	I	A_{520}	$\log K_1$	$\log K_{1(est)}$
0.0100	0.076	9.92	9.90	0.0100	0.610	9.16	9.19
0.0115	0.077	9.87	9.88	0.0175	0.607	9.14	9.10
0.0176	0.079	9.79	9.80	0.0250	0.593	9.04	9.02
0.0226	0.080	9.75	9.75	0.0320	0.577	8.94	8.97
0.0352	0.083	9.65	9.66	0.0482	0.566	8.87	8.87
0.0605	0.087	9.54	9.53	0.0630	0.548	8.77	8.79
0.1100	0.095	9.37	9.37	0.0881	0.531	8.67	8.70
0.1873	0.103	9.24	9.22	0.1133	0.517	8.59	8.62
0.2623	0.110	9.13	9.13	0.1641	0.499	8.49	8.49
				0.2130	0.484	8.40	8.40

Chromotrope 2B

I	A_{520}	$\log K_1$	$\log K_{1(est)}$
0.0100	0.513	9.05	9.04
0.0119	0.511	9.02	9.02
0.0160	0.508	8.98	8.98
0.0252	0.505	8.93	8.91
0.0435	0.499	8.85	8.82
0.0665	0.487	8.69	8.73
0.1124	0.482	8.62	8.61
0.1582	0.476	8.54	8.52
0.2271	0.468	8.43	8.42
0.2960	0.462	8.34	8.34

[a] ε_{HL} 1.5×10^3; ε_L 5.5×10^3; c_L 4.33×10^{-5} mol kg^{-1}; pH 8.66. [b] ε_{H_2L} 2.2×10^4; ε_{HL} 1.2×10^4; c_L 3.11×10^{-5} mol kg^{-1}; pH 8.66. [c] ε_{H_2L} 2.8×10^4; ε_{HL} 2.1×10^4; c_L 1.96×10^{-5} mol kg^{-1}; pH 8.66.

Table 2 Effect of increasing concentrations of $NaClO_4$ on the second protonation of T-azo-R,[a] and T-azo-C.[b] The ionic medium is $(H,Na)ClO_4$. I is in mol kg^{-1}.

T-azo-R				T-azo-C			
I	A_{490}	$\log K_2$	$\log K_{2(est)}$	I	A_{530}	$\log K_2$	$\log K_{2(est)}$
0.0010	0.228	3.07	3.07	0.0003	0.221	3.69	3.69
0.0051	0.250	2.97	2.96	0.0049	0.246	3.55	3.55
0.0102	0.266	2.90	2.90	0.0100	0.256	3.50	3.48
0.0506	0.313	2.68	2.67	0.0500	0.299	3.27	3.24
0.1000	0.335	2.56	2.55	0.1000	0.325	3.11	3.11
0.2000	0.358	2.41	2.43	0.2200	0.343	2.99	2.97
0.3000	0.366	2.36	2.37	0.3350	0.354	2.90	2.90
0.4000	0.369	2.34	2.35	0.4150	0.361	2.84	2.87
0.5200	0.371	2.32	2.33	0.5720	0.363	2.82	2.83
0.6600	0.370	2.33	2.34	0.8100	0.364	2.81	2.82
0.8900	0.367	2.35	2.37	0.9800	0.360	2.85	2.82
1.130	0.353	2.45	2.41	1.120	0.357	2.87	2.84

[a] ε_{H_2L} 1.0×10^3; ε_{HL} 9.0×10^3; c_L 4.87×10^{-5} mol kg^{-1}; pH 3.00. [b] ε_{H_3L} 2.0×10^3; ε_{H_2L} 9.0×10^3; c_L 4.66×10^{-5} mol kg^{-1}; pH 3.50.

When $c_L \gg c_M$, eqn. (8) holds.

Eqns. (7) and (8) hold if pure NY is the ionic medium. Here the ionic medium is (N,H,M)Y, but H and M are at low concentration compared with N, when the term containing the specific interaction coefficients becomes important. As described before for protonation, the value of the parameter $Z = mz_M^2 + pz_{H_xL}^2 - z_{M_mH_rL_p}^2 - qz_H^2$ is determined at low ionic strength, where the term containing the interaction coefficients is negligible. Once Z is known, $\log K_{Tc}$ and $S = mb(M,Y) + pb(H_xL,N) - b(M_mH_rL_p,Y,N) - qb(H,Y)$ are calculated from the straight line obtained by plotting $\log K_x + Z\, 0.51\, I^{\frac{1}{2}}/(1 + 1.5\, I^{\frac{1}{2}})$ *vs.* I.

Results and Discussion

Effect of Ionic Medium Concentration on Protonation Equilibria.—Chromotrope 2B is involved only in one protonation equilibrium in the acidity range pH = 2–11, while both T-azo-R and T-azo-C are involved in two. The absorption spectra of the differently protonated forms, and the protonation constants in 0.1 mol dm^3 sodium perchlorate, have been reported in previous papers.[10–12] The first protonation takes place at pH ~8–10, and the second one at pH 2.5–3.5. As an example, the effect of increasing concentration of $NaClO_4$ on these equilibria is shown in Tables 1 and 2, where the absorbances at fixed wavelength and different concentrations of salt are reported. From these data, the conditional protonation-constant values $\log K_x$ reported in Tables 1 and 2 were obtained. At low ionic strength the function $\log K_x$ *vs.* $0.51\, I^{\frac{1}{2}}/(1 + 1.5^{\frac{1}{2}})$ is a straight line, whose slope is $Z = z_H^2 + z_{H_{x-1}L}^2 - z_{H_xL}^2$. This derives from the fact that the term containing the specific interaction coefficients is negligible at low ionic strength. The values of Z at $I < 0.2$ mol kg^{-1} are reported in Table 3.

Then the thermodynamic protonation constants $\log K_{Tx}$ and $S = b(H,Y) + b(H_{x-1}L,N) - b(H_xL,N)$ were obtained.

The results are summarized in Table 3. The values of Z obtained experimentally can be compared with those estimated by considering the sulfonated azo dye as a particle with its charge evenly distributed over it, exactly like a small inorganic ion. The values so obtained are shown in Table 3 (estimated value of Z, global charge), and it is seen that the agreement with the experimentally found values is good. On the other hand, by considering the single charged sites as behaving independently, Z should be equal to 2 both for the first and the second protonation, which is completely different from the values found experimentally.

Therefore it is evident that the multiply charged organic ions considered here can be treated exactly like small inorganic anions.

These results agree with the findings of Salvatore and Ferri in the case of the many dicarboxylic acids they examined.[7] In contrast, in the case of some multiply charged indicators of the sulfophthaleinic and azo type, they found that each charge behaves independently.[6] However, it should be noted that they considered the data by Kilpatrick,[13] obtained only at ionic strength higher than 0.1 mol kg^{-1}, where the variations of the

$$\log K_c = \log \frac{\alpha_{H_xL} A - c_L\, \varepsilon_{H_xL'}}{\varepsilon_{M_mH_rL_p} c_L - A} - m \log c_M - q\,\mathrm{pH} = \log K_{Tc} - \frac{0.51\, I^{\frac{1}{2}}}{1 + 1.5\, I^{\frac{1}{2}}} (mz_M^2 + pz_{H_xL}^2 - z_{M_mH_rL_p}^2 - qz_H^2)$$
$$+ [mb(M,Y) + pb(H_xL,N) - b(M_mH_rL_p,Y,N) - qb(H,Y)]I \quad (7)$$

$$\log K_c = \log \frac{(\alpha_{H_xL} A - c_L\, \varepsilon_{H_xL}')\, \alpha_{H_xL}}{\varepsilon_{M_mH_rL_p}\, c_M \alpha_{H_xL} - (\alpha_{H_xL} A - c_L\, \varepsilon_{H_xL}')} - p \log c_L - q\,\mathrm{pH} = \log K_{Tc} - \frac{0.51\, I^{\frac{1}{2}}}{1 + 1.5\, I^{\frac{1}{2}}} (mz_M^2 + pz_{H_xL}^2 -$$
$$z_{M_mH_rL_p}^2 - qz_H^2) + [mb(M,Y) + pb(H_xL,N) - b(M_mH_rL_p, Y,N) - qb(H,Y)]I \quad (8)$$

Table 3 Protonation constants (K_{Tx}), sum of the squared charges (Z) and sum of the interaction coefficients (S) [eqn. (3)] for the protonation equilibria of T-azo-R, T-azo-C and Chromotrope 2B. Standard error of the estimated parameter is in parentheses.

	Z (estimated)		
	Global charge	Isolated sites	Z (obtained at low ionic strengths)
T-azo-R			
Proton reaction	$L^{4-} + H^+ \longleftrightarrow HL^{3-}$		
	8	2	7.49(0.19)
log K_{T1} 10.25(0.02)	S 0.24(0.03)		
Protonation reaction	$HL^{3-} + H^+ \longleftrightarrow H_2L^{2-}$		
	6	2	5.51(0.08)
log K_{T2} 3.16(0.01)	S 0.45(0.01)		
T-azo-C			
Proton reaction	$HL^{4-} + H^+ \longleftrightarrow H_2L^{3-}$		
	8	2	8.55(0.34)
log K_{T1} 9.55(0.03)	S −0.19(0.13)		
Protonation reaction	$H_2L^{3-} + H^+ \longleftrightarrow H_3L^{2-}$		
	6	2	5.71(0.13)
log K_{T2} 3.74(0.02)	S 0.31(0.01)		
Chromotrope 2B			
Proton reaction	$HL^{3-} + H^+ \longleftrightarrow H_2L^{2-}$		
	6	2	6.28(0.29)
log K_{T1} 9.31(0.02)	S −0.17(0.07)		

Table 4 Effect of increasing concentrations of $NaClO_4$ on the protonation of Methyl Orange[a] and Bromophenol Blue.[b] The ionic medium is $(H,Na)ClO_4$. I is in mol kg^{-1}.

Methyl Orange				Bromophenol Blue			
I	A_{525}	log K	log $K_{(est)}$	I	A_{589}	log K	log $K_{(est)}$
0.0003	0.673	3.79	3.75	0.0003	0.060	4.42	4.42
0.0053	0.660	3.75	3.71	0.0126	0.093	4.18	4.26
0.0100	0.653	3.73	3.69	0.0378	0.108	4.09	4.16
0.0200	0.635	3.69	3.68	0.0882	0.121	4.03	4.06
0.0425	0.628	3.67	3.66	0.1638	0.128	3.99	3.99
0.0650	0.634	3.68	3.67	0.2902	0.132	3.97	3.94
0.0875	0.635	3.69	3.67	0.6099	0.130	3.98	3.91
0.1370	0.638	3.70	3.71	0.8965	0.127	4.00	3.94
0.1860	0.647	3.72	3.74	1.226	0.117	4.05	3.99
0.2360	0.654	3.74	3.79	1.693	0.109	4.09	4.09
0.3750	0.723	3.93	3.93	2.207	0.097	4.15	4.22
0.5430	0.759	4.06	4.12				
0.7260	0.801	4.23	4.33				
1.000	0.851	4.52	4.66				
1.314	0.900	5.25	5.05				

[a] ε_{HL} 2.9 × 10^4; ε_L 6.5 × 10^3; c_L 3.19 × 10^{-5} mol kg^{-1}; pH 3.50; Z from data at low ionic strength 1.92(0.29) (expected from the global charge: 2); log K_T 3.78(0.08); S 1.30(0.05). [b] ε_{HL} 7.8 × 10^2; ε_L 6.6 × 10^4; c_L 7.72 × 10^{-6} mol kg^{-1}; pH 3.50; Z from data at low ionic strength: 4.07(0.65) (expected from the global charge: 4); log K_T 4.45(0.06); S 0.32 (0.02).

protonation constants due to the term containing Z are less significant, and this could cause a large uncertainty when estimating the value of Z.

To clarify this point, two of the multiply charged indicators studied by Salvatore *et al.*,[6] Methyl Orange (MO) and Bromophenol Blue (BPB), were re-examined here, by investigating with particular care the range of ionic strengths lower than 0.2 mol kg^{-1}. The absorbances of the solutions at different ionic strengths are shown in Table 4, together with the protonation constants obtained at each ionic strength. In these cases too log K_x depends linearly on $0.51\, I^{\frac{1}{2}}/(1 + 1.5\, I^{\frac{1}{2}})$ at ionic strength lower that ~0.2 mol kg^{-1}, with slope respectively 1.94 and 4.07, near to those expected by considering the global charge of the organic ion, *i.e.* 2 for MO and 4 to BPB, while 0 and 2 should be the Z-values if the charges were considered as distributed on isolated sites.

Table 5 Complexation constants (K_{Tc}), sum of the squared charges (Z) and sum of the interaction coefficients (S) [eqns. (7) and (8)] for the complexation of thorium with T-azo-R, T-azo-C and Chromotrope 2B in aq. sodium perchlorate. Standard error of the estimated parameter is in parentheses.

	Z (estimated)		
	Global charge	Isolated sites	Z (obtained at low ionic strengths)
T-azo-R			
Complexation reaction	$Th^{4+} + H_2L^{2-} \longleftrightarrow ThL + 2\,H^+$		
	18	10	10.28(1.43)
log K_{Tc} 1.50(0.05)	S 0.05(0.04)		
T-azo-C			
Complexation reaction	$Th^{4+} + H_3L^{2-} \longleftrightarrow ThH_2L^+ + H^+$		
	18	6	7.65(0.20)
log K_{Tc} 1.73(0.05)	S −0.27(0.02)		
Chromotrope 2B			
Complexation reaction (mononuclear complex)	$Th^{4+} + H_2L^{2-} \longleftrightarrow ThHL^+ + H^+$		
	18	6	6.10(0.38)
log K_{Tc} 1.81(0.01)	S −0.19(0.01)		
Chromotrope 2B			
Complexation reaction (binuclear complex)	$2\,Th^{4+} + H_2L^{2-} \longleftrightarrow Th_2L^{4+} + 2\,H^+$		
	18	12	13.27(1.15)
log K_{Tc} 4.85(0.07)	S 0.15(0.09)		

Tables 1, 2 and 4 report also the values of the conditional constants (log $K_{(est)}$) estimated on the basis of eqn. (3) with the proper parameters. The agreement with the experimental values is good.

Effect of the Ionic Medium Concentration on Complexation of Thorium by Sulfonated Azo Dyes.—The complexation of thorium with the azo dyes considered here has never been studied before. So the composition of complexes was first determined at constant ionic strength ($NaClO_4$ 0.1 mol kg^{-1}) by the graphical method of Sommer, which has been widely employed in previous investigations,[10–12] The complexation reactions are reported in Table 5.

T-azo-R and T-azo-C form complexes only with 1 : 1 metal to ligand molar composition, while Chromotrope 2B also forms a binuclear complex.

An example of the effect of increasing ionic strengths on these equilibria is shown in Table 6. These data were treated according to eqn. (7) or (8) and the results are reported in Table 5, which shows also the values of Z calculated by considering the global charge of the complex ion (Z expected, global charge). It is evident that the values of Z found experimentally are very different from those calculated in this hypothesis. Instead the complex ion can be considered as bearing two separate charged sites, one with a double negative charge, consisting of the sulfonic groups, and the other consisting of the chelated metal ion, with a charge corresponding to that of the cation minus the number of protons displaced. The values of Z obtained in this hypothesis are reported in Table 6 (Z expected, isolated sites), and they agree with those found experimentally.

The value of Z obtained in the case of the binuclear complex formed by Chromotrope 2B confirms that the linked metal ions act as independent charged sites. It agrees with the value calculated by considering that the charges on the sulfonic

Table 6 Effect of increasing concentrations of $NaClO_4$ on the complexation of thorium with T-azo-R and T-azo-C. The ionic medium is $(H,Na,Th)ClO_4$. I is in mol kg^{-1}.

T-azo-R[a]				T-azo-C[b]			
I	A_{530}	log K_c	log $K_{c(est)}$	I	A_{540}	log K_c	log $K_{c(est)}$
0.0300	0.034	0.88	0.80	0.0142	0.342	1.46	1.42
0.0494	0.031	0.65	0.65	0.0178	0.337	1.44	1.39
0.0686	0.028	0.48	0.54	0.0262	0.319	1.38	1.32
0.1010	0.025	0.34	0.41	0.0394	0.295	1.30	1.25
0.2210	0.020	0.15	0.10	0.0557	0.270	1.22	1.18
0.3410	0.015	−0.06	−0.07	0.0700	0.251	1.15	1.13
0.4460	0.012	−0.21	−0.18	0.0995	0.220	1.05	1.05
0.5720	0.011	−0.25	−0.28	0.1401	0.195	0.94	0.96
0.7550	0.009	−0.37	−0.39	0.1883	0.170	0.84	0.97
0.9780	0.007	−0.54	−0.48	0.2788	0.143	0.70	0.75
				0.4132	0.120	0.55	0.62
				0.5871	0.105	0.43	0.48
				0.7743	0.092	0.31	0.36
				1.093	0.081	0.17	0.19
				1.411	0.073	0.06	0.04
				1.840	0.065	−0.07	−0.13

Chromotrope 2B (mononuclear complex)[c]				Chromotrope 2B (binuclear complex)[d]			
I	A_{600}	log $K_{c1,1}$	log $K_{c1.1(est)}$	I	A_{600}	log $K_{c2.1}$	log $K_{c2,1(est)}$
0.0098	0.467	1.52	1.54	0.0280	0.208	4.16	4.04
0.0879	0.364	1.18	1.17	0.1095	0.137	3.44	3.51
0.2108	0.305	0.94	0.94	0.2142	0.097	3.12	3.21
0.4262	0.263	0.71	0.72	0.4139	0.070	2.86	2.91
0.6377	0.245	0.57	0.58	0.6093	0.061	2.76	2.74
0.9904	0.228	0.40	0.40	0.9737	0.050	2.60	2.56
1.349	0.217	0.25	0.25	1.482	0.043	2.47	2.44
1.825	0.208	0.09	0.09	1.994	0.041	2.43	2.38

[a] ε_{H_2L} 0; ε_{HL} 4.54 × 10^2; ε_{ThL} 3.68 × 10^3; pH 2.00; c_L 1.06 × 10^{-5} mol kg^{-1}; c_{Th} 1.02 × 10^4 mol kg^{-1}. [b] ε_{H_3L} 1.19 × 10^3; ε_{H_2L} 5.05 × 10^3; ε_{Th_2L} 1.86 × 10^4; pH 2.03; c_L 2.95 × 10^{-5} mol kg^{-1}; c_{Th} 4.92 × 10^{-4} mol kg^{-1}. [c] ε_{H_2L} 6.1 × 10^2; ε_{ThHL} 1.7 × 10^4; c_L 3.07 × 10^{-4} mol kg^{-1}; c_{Th} 3.15 × 10^{-5} mol kg^{-1}; pH 2.01. [d] ε_{H_2L} 6.1 × 10^2; ε_{Th_2L} 7.8 × 10^3; c_L 3.07 × 10^{-5} mol kg^{-1}; c_{Th} 6.30 × 10^{-4} mol kg^{-1}; pH 1.51.

Table 7 Complexation constants (K_{Tc}), sum of the squared charges (Z) and sum of the interaction coefficients (S) [eqn. (7)] for the complexation equilibria of indium with T-azo-R and T-azo-C. Standard error of the estimated parameter is in parentheses.

	Z (estimated)		Z (obtained at low ionic strengths)
	Global charge	Isolated sites	
T-azo-R			
Complexation reaction	$In^{3+} + H_2L^{2-} \longleftrightarrow InL^- + 2H^+$		
	10	6	5.34(0.23)
log K_{Tc} 0.06(0.06)	S −0.16(0.02)		
T-azo-C			
Complexation reaction	$In^{3+} + H_3L^{2-} \longleftrightarrow InHL^- + 2H^+$		
	10	6	5.34(0.31)
log K_{Tc} −2.54(0.07)	S 0.00(0.03)		

groups and on each bound metal ion behave as separate sites. In this case $Z = 12$ was calculated, with $Z = 18$ by considering the global charge of the complex and $Z = -6$ if the charges on the linked metal ions are considered together. The agreement between the experimental conditional complexation constants and those estimated with $Z = 12$, and the other parameters reported in Table 5 (log $K_{c(est)}$), which are also shown in Table 6, is good.

Table 8 Effect of increasing concentrations of $NaClO_4$ on the complexation of indium with T-azo-R[a] and T-azo-C.[b] The ionic medium is $(H,Na,In)ClO_4$. I is in mol kg^{-1}.

T-azo-R				T-azo-C			
I	A_{520}	log K_c	log $K_{c(est)}$	I	A_{560}	log K_c	log $K_{c(est)}$
0.0100	0.773	−0.25	−0.20	0.0037	0.164	−2.76	−2.71
0.0159	0.740	−0.36	−0.27	0.0115	0.149	−2.83	−2.82
0.0307	0.711	−0.43	−0.37	0.0192	0.127	−2.96	−2.89
0.0533	0.672	−0.52	−0.47	0.0268	0.117	−3.01	−2.94
0.0820	0.634	−0.59	−0.57	0.0394	0.107	−3.06	−3.01
0.1140	0.601	−0.65	−0.64	0.0502	0.099	−3.11	−3.05
0.1822	0.547	−0.75	−0.76	0.0775	0.088	−3.17	−3.14
0.3118	0.472	−0.88	−0.92	0.1021	0.082	−3.20	−3.20
0.4632	0.423	−0.97	−1.04	0.1510	0.072	−3.27	−3.29
0.6622	0.365	−1.09	−1.17	0.2000	0.066	−3.31	−3.36
0.9317	0.305	−1.24	−1.30	0.3080	0.056	−3.41	−3.47
1.210	0.259	−1.37	−1.40	0.4470	0.051	−3.47	−3.56
1.470	0.226	−1.48	−1.49	0.6150	0.047	−3.54	−3.64
1.800	0.188	−1.61	−1.59	0.8200	0.044	−3.60	−3.71
2.120	0.162	−1.72	−1.68	1.026	0.041	−3.68	−3.77
2.653	0.126	−1.88	−1.81	1.272	0.036	−3.84	−3.82
				1.541	0.034	−3.92	−3.87
				1.808	0.032	−4.00	−3.90

[a] ε_{H_2L} 1.0 × 10^2; ε_{HL} 1.50 × 10^3; ε_{InL} 1.6 × 10^4; c_L 5.64 × 10^{-5} mol kg^{-1}; c_{In} 5.62 × 10^{-4} mol kg^{-1}; pH 2.17. [b] ε_{H_3L} 2.1 × 10^2; ε_{H_2L} 1.0 × 10^3; ε_{InL} 9.1 × 10^3; c_L 3.11 × 10^{-5} mol kg^{-1}; c_{In} 4.99 × 10^{-4} mol kg^{-1}; pH 3.15.

Table 9 Effect of increasing concentrations of $NaClO_4$ on the complexation of copper(II) with T-azo-R.[a] The ionic medium is $(H,Na,Cu)ClO_4$. I is in mol kg^{-1}.

I	A_{535}	log K_c	log $K_{c(est)}$
0.0316	0.352	0.86	0.88
0.0444	0.351	0.86	0.86
0.0568	0.345	0.84	0.85
0.0694	0.342	0.83	0.83
0.0920	0.339	0.82	0.82
0.0947	0.336	0.81	0.81
0.107	0.332	0.80	0.80
0.132	0.326	0.78	0.78
0.156	0.320	0.77	0.76
0.181	0.316	0.76	0.76
0.293	0.299	0.71	0.70
0.469	0.279	0.67	0.64
0.679	0.258	0.62	0.59
0.912	0.236	0.56	0.55
1.15	0.219	0.52	0.51
1.39	0.200	0.46	0.47
1.66	0.183	0.41	0.43

[a] ε_{H_2L}0; ε_{HL} 2.7 × 10^2; ε_{CuL} 1.7 × 10^4; c_L 3.08 × 10^{-5} mol kg^{-1}; c_{Cu} 3.02 × 10^{-4} mol kg^{-1}; pH 1.50; Z from the data at low ionic strength: 1.75(0.11); log K_{Tc} 1.03(0.01); S −0.09(0.01).

Effect of Ionic Medium Concentration on Complexation of Indium with Sulfonated Azo Dyes.—The complexation of the considered sulfonated azo dyes with indium in 0.1 mol dm^{-3} sodium perchlorate was studied previously.[14] The complexation reactions are shown in Table 7.

Chromotrope 2B does not form any complex with indium in aqueous solution. The effect of increasing concentrations of sodium perchlorate on these complexation equilibria is shown in Table 8, which reports the absorbance measured at a wavelength where the complex absorbs more than the free ligand. The conditional complexation constants at each ionic strength are also shown. These data were treated according to eqn. (7) in order to determine the parameters. The results are reported in Table 7. The value of Z calculated by considering the global charge on the complexes (−1) is 10. Evidently this is not in agreement with the experimentally found values. A better fitting was obtained when two separate charged sites are considered, one with charge +1, corresponding to the chelated metal ion, and the other with charge −2, corresponding to the sulphonic groups of the ligand. The value $Z = 6$ calculated in this hypothesis is near to the experimentally found value. The conditional complexation constants estimated are also reported in Table 8, and it is seen that they agree well with the experimental values.

Effect of Ionic Medium Concentration on Complexation of Copper with Sulfonated Azo Dyes.—It should be noted that in many cases only one value is expected for Z either in the hypothesis of the global charge or of the separate sites. This happens when the chelation site is neutral. For instance this is the case for the complexation of T-azo-R with copper(II), according to the equilibrium $Cu^{2+} + H_2L^{2-} \longleftrightarrow CuL^{2-} + 2H^+$ for which $\log K = 0.80$ was determined in 0.1 mol dm^3 sodium perchlorate in a previous investigation.[10] The conditional constants at different sodium perchlorate concentrations, obtained by the usual method, are reported in Table 9. The parameters $\log K_{Tc}$, Z and S, evaluated according to eqn. (7), are also shown in Table 9. The experimentally found value of Z agrees with the value estimated, which can be only 2, since the complexation site is neutral, as copper with two positive charges displaces two protons. Table 9 also shows values for $\log K_{c(est)}$, which are the values estimated from the parameters and agree well with the experimental values.

Conclusions

The conditional protonation and complex formation constants of sulfonated azo dyes at different ionic strength can be estimated from the thermodynamic constants by evaluating the activity coefficients with an equation derived from Specific Interaction Theory, on the hypothesis that the specific interaction coefficients are independent of the ionic medium concentration. Agreement between the conditional constants estimated and those obtained experimentally is better than 0.1 in $\log K$.

It has been shown that the charge of the bisulfonated azo dyes must be considered as globally distributed on the molecule, while the complex ions, containing metals, behave as if they bear different charged sites, corresponding respectively to the complexation sites where the metal ion is linked, and to the residual charge of the ligand. This could indicate either a purely electrostatic, coordinative interaction between the metal ion and the phenolic oxygen, strictly localized at the complexation site, or an outer-sphere ion-pairing.

The other important point when dealing with solutions at ionic strength higher than ~0.2 mol kg^{-1} is the summation of the specific interaction coefficients (S) of the ions involved. Its estimation can easily be done experimentally, if the specific interaction coefficients are unknown. It would be highly desirable if these data, obtained by determination of the conditional equilibrium constants at at least two different ionic strengths, were to be reported in all the papers dealing with equilibrium analysis.

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