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Interaction of Zn(II) and Cd(II) with Large Polyazacycloalkanes in dmso/H_2O (80:20 vol./vol.). A Potentiometric Study

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Abstract

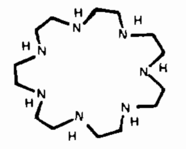
A potentiometric study on the interaction at 25 °C and 0.15 mol dm^{-3} between large polyazacycloalkanes of the series [3k]aneN_k and Zn(II) and Cd(II) ions in dmso:H_2O (80:20 vol./vol.) is reported. The protonation behavior of the free macrocycles and coordination trends are compared with those previously observed in aqueous solution. The main features observed in the mixed solvent are: similar protonation behavior of the free polyamines, greater tendency to form binuclear and protonated complexes and a lower tendency to bear hydrolytic reactions.

Introduction

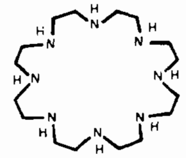
Formation studies on metal complexes of large polyazacycloalkanes of the series [3k]aneN_k (k = 7–12) reveal that the ability of these ligands to form polynuclear complexes depends both on the size of the macrocycle and on the characteristics of the metal ion [1–7]. As the macrocycle size increases the stabilities of the mononuclear complexes decrease and those of the binuclear complexes increase. Therefore, the smaller macrocycles only form mononuclear species while the larger ones only form binuclear complexes. For all the metal ions studied up to now at least one macrocycle for which both mono- and binuclear species coexist has been found. The size and number of nitrogen donors of the macrocycle, affording this intermediate behavior, depends on the metal ion. As a matter of fact, for cobalt(II) [4] the macrocycle [27]aneN_9, containing nine nitrogen donors available, is the smallest [3k]aneN_k ligand able to form binuclear complexes, while for zinc(II) [3], cadmium(II) and nickel(II) [5, 7] eight nitrogen donors ([24]aneN_8) are required to display this behavior. In the case of copper(II) the intermediate system corresponds to the smaller [21]aneN_7 [1a]. Furthermore, this is the only metal ion which forms trinuclear complexes with the larger macrocycles of the series [33]aneN_{11} and [36]aneN_{12} [1e].

Until the present moment, all these equilibrium studies had been carried out in aqueous medium. It has been proved that at least in the majority of binuclear complexes, not all the coordination sites of the metal are fulfilled by the nitrogen donors of the macrocycle. Thereby, from a change of solvent, not just effects derived from a different solvation (second coordination sphere) but also effects induced by a direct interaction with the metal ion (first coordination sphere) are to be expected.

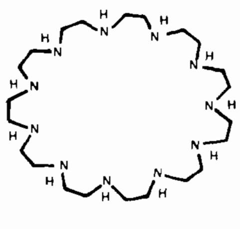
In the present work the interaction between zinc(II) and cadmium(II) ions and some of these large polyazacycloalkanes in the solvent mixture dmso–water (80:20, vol./vol.) has been studied.



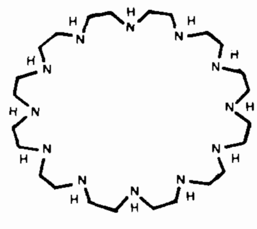
[21]aneN_7



[24]aneN_8



[33]aneN_{11}



[36]aneN_{12}

Experimental

Reagents

The synthesis of the ligands [21]aneN_7, [24]aneN_8, [33]aneN_{11} and [36]aneN_{12} has been carried

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TABLE 1. Logarithms of the stepwise protonation constants of macrocycles $[3k]\text{aneN}_k$ in 0.15 mol dm^{-3} $KClO_4$ dmso–water (80:20 vol./vol.) and in 0.15 mol dm^{-3} $NaClO_4$ aqueous solution at 25 °C

Reaction[a]	[21]aneN$_7$		[24]aneN$_8$		[33]aneN$_{11}$		[36]aneN$_{12}$	
	H_2O	H_2O/dmso	H_2O	H_2O/dmso	H_2O	H_2O/dmso	H_2O	H_2O/dmso
$L + H = HL$		10.12(1)[b]		10.11(1)		10.17(2)		10.23(1)
$L + 2H = H_2L$		19.36(1)		19.49(1)		19.81(1)		19.87(1)
$L + 3H = H_3L$		27.54(1)		27.96(1)		28.83(1)		28.89(2)
$L + 4H = H_4L$		33.74(1)		35.58(1)		37.03(1)		37.36(1)
$L + 5H = H_5L$		37.50(1)		40.19(4)		44.93(1)		45.17(2)
$L + 6H = H_6L$		39.46(1)		42.98(2)		51.24(1)		52.34(2)
$L + 7H = H_7L$						55.63(1)		57.67(2)
$L + 8H = H_8L$						58.89(1)		61.48(2)
$L + 9H = H_9L$						61.40(3)		64.30(3)
$L + 10H = H_{10}L$						63.87(2)		66.1(1)
$H + L = HL$	9.83[c]	10.12	10.01[c]	10.12	9.79[d]	10.17	9.75[c]	10.23
$H + HL = H_2L$	9.53	9.24	9.50	9.38	9.48	9.64	9.65	9.65
$H + H_2L = H_3L$	8.84	8.18	9.10	8.46	9.02	9.01	8.88	9.02
$H + H_3L = H_4L$	6.72	6.20	8.29	7.62	8.64	8.20	8.96	8.47
$H + H_4L = H_5L$	4.04	3.76	5.01	4.61	8.06	7.90	8.12	7.81
$H + H_5L = H_6L$	2.43	1.96	3.71	2.79	6.44	6.32	7.82	7.17
$H + H_6L = H_7L$	2.30		2.98		4.49	4.38	5.66	5.34
$H + H_7L = H_8L$			1.97		3.58	3.27	4.27	3.81
$H + H_8L = H_9L$					2.76	2.51	3.58	2.82
$H + H_9L = H_{10}L$					2.26	2.47	2.62	1.8
$H + H_{10}L = H_{11}L$					1.7		2.3	
$H + H_{11}L = H_{12}L$								

[a] Charges omitted for clarity. [b] Values in parentheses are standard deviations in the last significant figure. [c] Taken from ref. 3. [d] Taken from ref. 5.

out as previously reported [1]. Stock solutions of $Cd(NO_3)_2 \cdot 4H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ (Merck p.a.) in double distilled water were standardized by potentiometric titration with EDTA [8]. HCl and CO_2-free NaOH solutions were prepared and standardized as previously described [9]. Dimethyl sulfoxide (dmso) was purified by distillation under reduced pressure (*c.* 2 Torr (266 Pa)) and stored in a dark bottle over 4 Å molecular sieves. From this solvent the dmso–water mixture (80:20 vol./vol.) was prepared. All the solutions used in the potentiometric study were prepared in order to have the indicated dmso–water volume ratio. $KClO_4$ (Merck p.a.) was used to keep the ionic strength constant at 0.15 mol dm^{-3}.

e.m.f. Measurements

The potentiometric titrations were carried out using equipment (potentiometer, buret, stirrer, microcomputer, etc.) that has already been described [10]. The GK 2401C combined glass electrode used was dipped in dmso–water (80:20 vol./vol.) for 30 min before use. The standard potential of the electrode, E°, was determined by the Gran method [11]. Nernst's equation was strictly obeyed by the electrode in this medium. The value obtained for pK_W in the mixed solvent was 18.60(2). The computer program SUPERQUAD [12] was used to process e.m.f. data and calculate both basicity and stability constants.

Method

At least two potentiometric titrations were carried out for each system. The titration curves, for a system, were treated either as a single set or as separated entities without significant variation in the stability constants. Tentative species introduced to test the consistency of other models, by the procedure reported in footnote 18 of ref. 1e, were rejected.

Results and Discussion

Protonation of the Ligands

In Table 1 the protonation constants of the polyazacycloalkanes studied here in dmso–water (80:20 vol./vol.) together with those previously determined in aqueous solution are reported. The first stepwise protonation constants are similar in both solvents, these polyamines being slightly more basic in dmso–water which could be attributed to different solvation either of the free amines and of the hydrogen ions. In the following protonation steps the basicity in dmso–

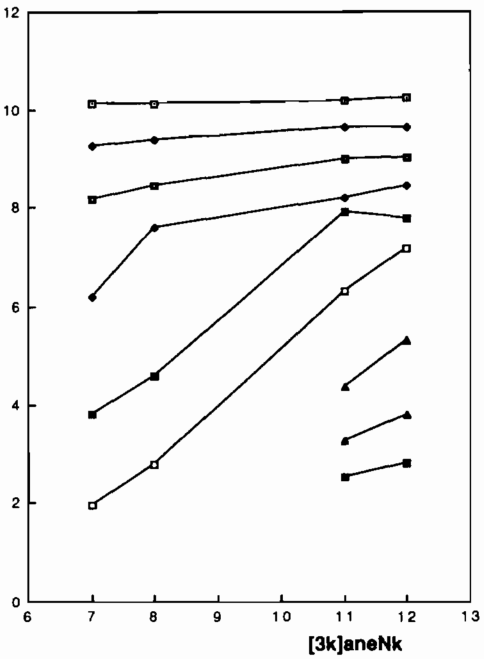
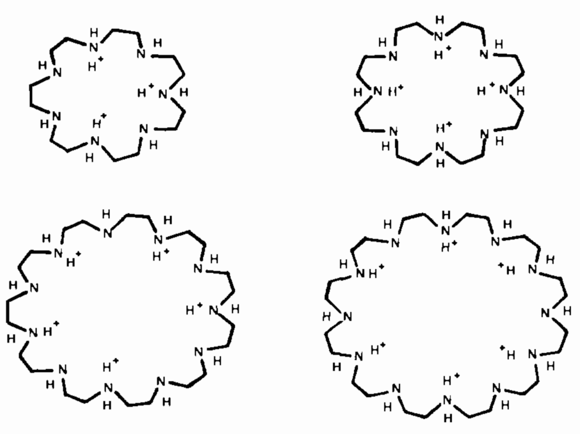


Fig. 1. Plot of the stepwise protonation constants obtained in dmso–water (80:20 vol./vol.) vs. the number of nitrogen atoms in the macrocycles (from the top: $L + H = HL$, $H + HL = H_2L$, $H + H_2L = H_3L$, $H + H_3L = H_4L$, $H + H_4L = H_5L$, $H + H_5L = H_6L$, $H + H_6L = H_7L$, $H + H_7L = H_8L$, $H + H_8L = H_9L$).

water drops down faster than in water, to such an extent that the last protonation constants could not be determined under the experimental condition employed. As the dielectric constant of this mixed solvent is lower than that of water, the ability to reduce the electrostatic repulsion between the positive charges on the macrocyclic framework is smaller and consequently, the basicity decreases faster.

The grouping of the protonation constants, which had already been observed in aqueous solution, is still maintained in this mixed solvent (Fig. 1) because it mainly depends on the cyclic nature of the ligands. To explain this grouping effect, both the number of nitrogen atoms and their disposition in each of the macrocycles have to be taken into account. The maximum number of protons that a macrocycle can take up without a great increase in electrostatic repulsion is schematized below. For a generic $[3k]$aneN$_k$ macrocycle this number is $k/2$ when k is even and $(k - 1)/2$ when k is odd. Additional protonation of a nitrogen atom would yield rather different effects for even or odd values of k. If k is even, the $(k/2 + 1)$th proton is constrained to the location between two neighboring protonated nitrogens, while, when k is odd, two non-protonated adjacent nitrogens are available for the $[(k - 1)/2 + 1]$th proton. In the first case a greater electrostatic repulsion, and consequently a more remarkable decrease in basicity, is produced. The difference between both groups of constants is greater for smaller macrocycles than for larger ones, which can be attributed, among other factors such as conformation and hydrogen bonding, to a greater charge density in the smaller macrocycles.



Solution Equilibria of Zinc(II) and Cadmium(II) Complexes

In the present work we have investigated the formation of complexes between the large polyazacycloalkanes [21]aneN$_7$, [33]aneN$_{11}$ and [36]aneN$_{12}$ and zinc(II) as well as between [24]aneN$_8$ with both zinc(II) and cadmium(II) ions in the solvent mixture dmso/H_2O (80:20 vol./vol.). This mixture has been chosen as a solvent in order to study the changes brought about by a different medium on the coordination features of large polyazacycloalkanes. In fact, dmso is an aprotic and polar solvent; its dielectric constant is 48.9 while that of water is 78.5. It is a good coordinating agent for cations, but not for anions [13]. In spite of the high content in water, the extent of the hydrolysis of the metal ions is much lower in this mixed solvent than in water. So, solutions of iron(III) salts in dmso–water (80:20) are indefinitely stable, remaining practically unhydrolysed [14].

It is well known that zinc(II) amine complexes show a great tendency to undergo hydrolytic reactions in water solutions. In previous works it has been shown that zinc(II)–$[3k]$aneN$_k$ binuclear complexes have a special ability to form hydroxo species [15]. This tendency increases as the macrocycle becomes smaller to such an extent that, in the case of [24]aneN$_8$, this hydrolysis prevents the formation of nonhydroxylated binuclear species, $[Zn_2([24]aneN_8)OH]^{3+}$ being the only binuclear species present in solution.

In Table 2 the equilibrium constants for the formation of zinc(II) and cadmium(II) complexes with the $[3k]$aneN$_k$ ligands studied here in dmso–water (80:20 vol./vol.) are reported together with

TABLE 2. Logarithms of the stability constants for the formation of complexes between Zn(II) and Cd(II) ions and the macrocycles [3*k*]aneN$_k$ in 0.15 mol dm^{-3} $KClO_4$ dmso–water (80:20 vol./vol.) and in 0.15 mol dm^{-3} $NaClO_4$ aqueous solution at 25 ℃

Reaction[a]	[21]aneN$_7$		[24]aneN$_8$		[33]aneN$_{11}$		[36]aneN$_{12}$	
	H_2O	H_2O/dmso	H_2O	H_2O/dmso	H_2O	H_2O/dmso	H_2O	H_2O/dmso
Zn + L = ZnL	13.33[b]	17.54(3)[c]	13.49[b]	14.04(2)				
Zn + L + H = ZnHL		23.50(2)		22.49(2)				
Zn + L + 2H = ZnH_2L		28.01(3)						
Cd + L = CdL			14.52[d]	17.86(2)				
Cd + L + H = CdHL				23.85(3)				
Cd + L + 2H = CdH_2L				29.73(2)				
Cd + L + 3H = CdH_3L				34.85(3)				
2Zn + L = Zn_2L				23.73(1)	23.91[b]	28.12(1)	26.27[b]	32.25(1)
2Zn + L + H = Zn_2HL				28.62(1)		34.96(1)		37.77(1)
2Zn + L + 2H = Zn_2H_2L				33.59(1)		40.73(1)		42.67(2)
2Zn + L + 3H = Zn_2H_3L						45.17(1)		47.67(3)
2Zn + L + 4H = Zn_2H_4L						49.61(1)		51.78(5)
2Zn + L + 5H = Zn_2H_5L								55.96(3)
2Zn + L + H_2O = Zn_2LOH + H				13.49(2)		16.75(1)		
2Cd + L = Cd_2L			18.21[d]	22.21(3)				
2Cd + L + H = Cd_2HL				27.38(5)				
ZnL + H = ZnHL	6.7[b]	6.0	8.6[b]	8.5				
ZnHL + H = ZnH_2L	4.9[b]	4.5	5.5[b]					
CdL + H = CdHL			7.2[d]	6.0				
CdHL + H = CdH_2L			5.9[d]	5.9				
ZnL + OH = ZnLOH	2.0[b]		3.1[b]					
Zn_2L + H = Zn_2HL				4.9		6.8	6.6[b]	5.5
Zn_2HL + H = Zn_2H_2L				5.0		5.8	6.3[b]	4.9
Zn_2H_2L + H = Zn_2H_3L					5.5[b]	4.4	5.7[b]	5.0
Zn_2H_3L + H = Zn_2H_4L						4.4	5.2[b]	4.1
Zn_2H_4L + H = Zn_2H_5L								4.2
Cd_2L + H = Cd_2HL				5.2				
Zn_2L + H_2O = Zn_2LOH + H				–10.2	–8.5[b]	–11.4	–10.2[b]	
Zn_2L + OH = Zn_2LOH				8.5	5.2[b]	7.4	3.5[b]	

[a] Charges omitted for clarity. [b] Taken from ref. 3. [c] Values in parentheses are standard deviations in the last significant figure. [d] Taken from ref. 1e.

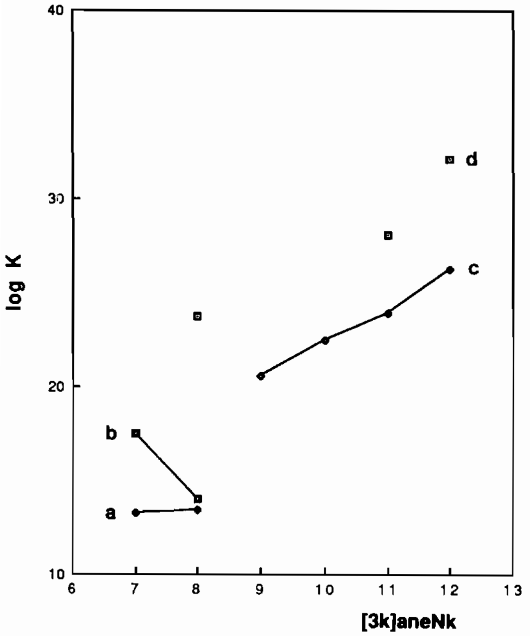


Fig. 2. Plot of the stability constants obtained in water and dmso–water (80:20 vol./vol.) vs. the number of nitrogens in the macrocycle. a, M + L = ML (water); b, M + L = ML (dmso–water (80:20 vol./vol.)); c, 2M + L = M_2L (water); d, 2M + L = M_2L (dmso–water (80:20 vol./vol.)).

those previously determined in water for the corresponding systems.

Zinc(II) forms, under our experimental condition, only mononuclear complexes with [21]aneN_7, while both mono- and binuclear complexes are formed with [24]aneN_8. For the larger macrocycles [33]aneN_{11} and [36]aneN_{12} only binuclear species have been detected. As shown in Fig. 2, the number of nitrogen donors on the macrocycle produces opposite effects on the stability of mononuclear and binuclear species. In fact, mononuclear complexes display a decreasing stability when passing from [21]aneN_7 to [24]aneN_8, while the stability of binuclear complexes increases with the number of nitrogen donors of the macrocycle. This behavior can be readily rationalized taking into account that [21]aneN_7 has more than enough nitrogens to complete the coordination sphere of the metal ion. Thereby, when passing to [24]aneN_8, a decrease due to the formation of larger chelate rings is to be expected. On the other hand, for the binuclear complexes, an increase in the number of nitrogen atoms of the macrocycle also implies an increase in the number of Zn–N bonds producing higher stability. Furthermore, a greater number of coordinated nitrogens causes a reduction in the electrostatic repulsion between both metal centers.

In Fig. 2 the stability constants determined in both solvents, water and dmso–water (80:20 vol./vol.), are compared. It is worth noting that all the complexes are more stable in this mixed solvent than in water except in the case of [24]aneN_8 for which the stability difference is small.

The high number of donor atoms present in the macrocyclic framework of these ligands allows the formation of many protonated complex species. The complex $[Zn_2([36]aneN_{12})]^{4+}$ can bind up to five protons producing the highly charged species $[Zn_2H_5([36]aneN_{12})]^{9+}$ in which only seven nitrogen atoms are available for coordination to the two zinc(II) ions. With [33]aneN_{11} protonated binuclear complexes up to $[Zn_2H_4([33]aneN_{11})]^{8+}$ have been detected. Similarly, in this complex the number of available nitrogens for coordination is seven. In the case of [24]aneN_8 six nitrogen atoms would be enough to coordinate two zinc(II) ions as shown by the formation of the diprotonated species $[Zn_2H_2([24]aneN_8)]^{6+}$. These features indicate again the great flexibility of these polyazacycloalkanes which can rearrange their conformation to occupy more coordination sites as the protons are released. The stepwise protonation constants of the binuclear metal complexes are relatively low if compared with those of the free ligand. This can be associated with the breaking of M–N bonds in the protonation reactions of the complexes. Only in the case of mononuclear complexes are some of these constants higher. For instance, the equilibrium constant relative to the protonation of $[Zn([24]aneN_8)]^{2+}$, in which uncoordinated nitrogen atoms are present, to give $[ZnH([24]aneN_8)]^{3+}$ ($\log K = 8.45$) is equal, within experimental error, to that obtained for the protonation of the diprotonated form of the ligand ($\log K = 8.46$) to obtain $[H_3([24]aneN_8)]^{3+}$. This result indicates that the free nitrogen bearing protonation in $[ZnH([24]aneN_8)]^{3+}$ has to be located far away from the metal ion.

The stepwise protonation constants of the zinc(II) complexes are lower in the mixed solvent than in water as a consequence of the higher stability of these complexes in the mixed solvent. However, more protonated species are formed in dmso–water (80:20 vol./vol.) than in water. Unlike the formation of these protonated species, the formation of unprotonated complexes predominates in a wide pH range, as shown in Fig. 3 for the system zinc(II)/[24]aneN_8.

At higher pH values, for the ligands [24]aneN_8 and [33]aneN_{11}, the monohydroxo dimetal complexes $[Zn_2([24]aneN_8)(OH)]^{3+}$ and $[Zn_2([33]aneN_{11})(OH)]^{3+}$ have been detected. The hydrolysis constants are lower in this mixed solvent than in water. For [21]aneN_7 and [36]aneN_{12} hydroxo species have not been observed, which might be due to the fulfilling of the zinc(II) coordination sites by the nitrogen donors of these ligands. A significant difference induced by the solvents can be observed in the system zinc(II)/[24]aneN_8. If the distribution diagrams determined in both solvents for a 1:1 metal/

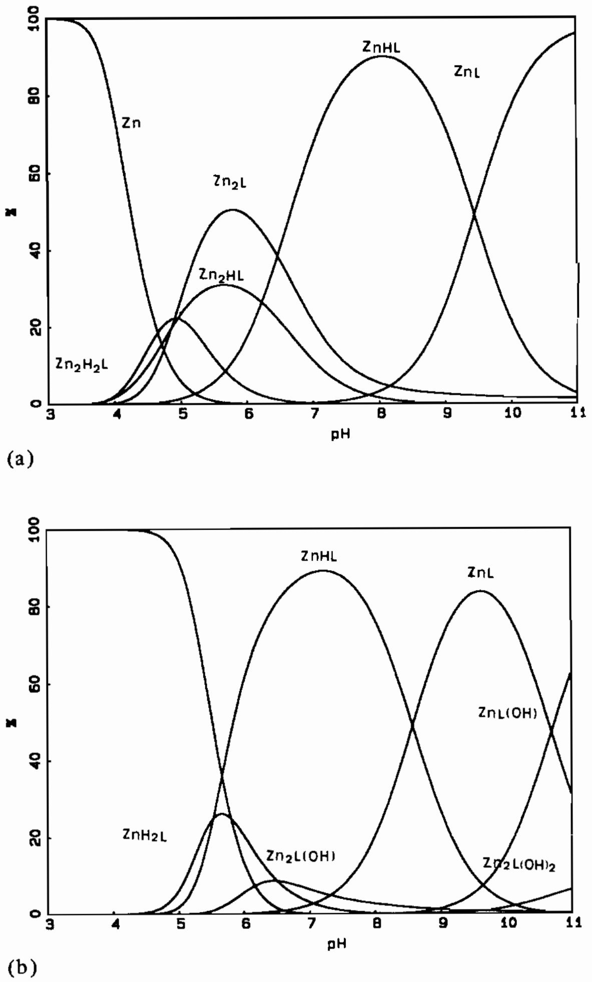


Fig. 3. Calculated distribution of the equilibrium species formed in the system Zn^{2+}/[24]aneN_8 at 25 °C: (a) 10^{-3} mol dm^{-3} Zn^{2+} and [24]aneN_8 (dmso/water (80:20 vol./vol.)) in 0.15 mol dm^{-3} $KClO_4$; (b) 10^{-3} mol dm^{-3} Zn^{2+} and [24]aneN_8 (water) in 0.15 mol dm^{-3} $NaClO_4$.

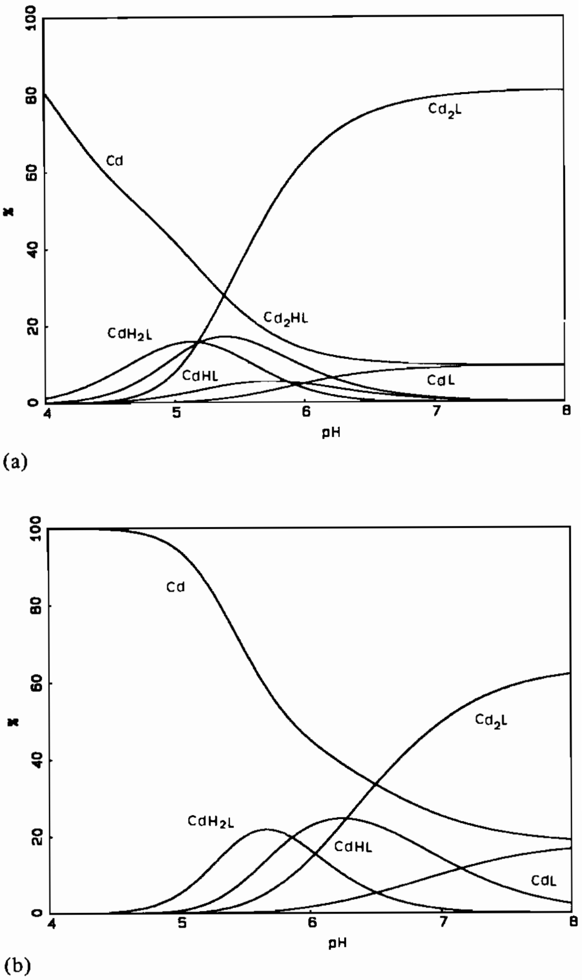


Fig. 4. Calculated distribution of the equilibrium species formed in the system Cd^{2+}/[24]aneN_8 at 25 °C: (a) 2×10^{-3} mol dm^{-3} Cd^{2+} and 10^{-3} mol dm^{-3} [24]aneN_8 (dmso/water (80:20 vol./vol.)) in 0.15 mol dm^{-3} $KClO_4$; (b) 2×10^{-3} mol dm^{-3} Cd^{2+} and 10^{-3} mol dm^{-3} [24]aneN_8 (water) in 0.15 mol dm^{-3} $NaClO_4$.

ligand ratio are compared (Fig. 3), it can be observed that in water solution the predominant species are the mononuclear ones, while $[Zn_2([24]aneN_8)(OH)]^{3+}$ is formed in a very low percentage. In dmso–water the predominant species are the binuclear ones up to slightly alkaline solutions where the mononuclear species start to predominate. Therefore, a stabilization of the binuclear species with respect to the mononuclear ones in the mixed solvent occurs.

Since the influence of the solvent seems to be very important in these intermediate systems, the formation of cadmium(II) complexes with [24]aneN_8 was studied. The results obtained for this system are reported in Table 2. A comparison between the distribution diagrams determined for a 2:1 cadmium(II)/[24]aneN_8 ratio in both solvents (Fig. 4) again shows a stabilization of the binuclear complexes in the mixed solvent with respect to mononuclear complexes. The ratio between the stability constants of the binuclear complexes and mononuclear complexes is higher in the mixed solvent.

The formation of complexes by [3*k*]aneN_k macrocycles in the mixed solvents takes place at lower pH values than in water, due to the smaller overall basicity of these ligands. These results, together with the higher stability of the complexes in dmso–water, are promising for the investigation of the solution chemistry of highly acid metal ions such as iron(III) whose study in water solution is prevented by hydrolytic reactions.

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