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Study of the Coordination Properties of 1,2-Bis(2,6-dimethphenylamino) Glyoxime and Determine the Stability Constant of Its Complexes with Ni(II), Cu(II) and Zn(II) Metal Ions in Solution

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Abstract This study aims to investigate the nature and type of complexes formed in solution between 1,2-bis(2,6-dimethphenylamino) glyoxime (DPG) and the ions Ni^{2+}, Cu^{2+} and Zn^{2+}. Potentiometric titration was used to follow the formation of complexes.

The complexes formed were studied through the determination of stability constants of these complexes in mixed ethanol–aqueous solution at 25 ± 0.1 °C and ionic strength of 0.1 mol·dm^{-3} NaCl. The basicity of the ligand was also assessed by the determination of the dissociation constants of the ligand. All of the constants were determined by computer refinement of pH–volume data using the SUPERQUAD program. The species distribution diagrams were also calculated.

Comparison with other vic-dioximes was made to provide reliable support for the formation of the proposed complexes in solution.

Keywords Vic-dioxime · Potentiometric titration · Metal complexes · Stability constants · SUPERQUAD · Dissociation constants

1 Introduction

The basis for the wide use of vic-dioxime metal complexes is their outstanding stability [1]. Vic-dioximes, together with their complexes, are of interest for many researchers in different fields of chemistry. They have enormous importance in coordination chemistry, as many complexes of vic-dioximes with transition metal ions have been isolated and characterized [2]. The presence of the acidic hydroxyl group and the basic azomethine group in

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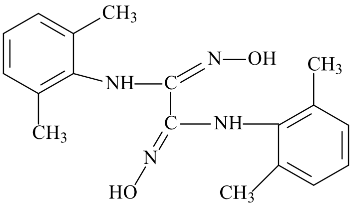

Fig. 1 1,2-bis(2,6-dimethylphenylamino) glyoxime

the vic-dioxime molecule makes it a suitable ligand for coordination with a variety of metal ions. The great stability of some vic-dioximes, such as dimethyl glyoxime (DMG), is associated with the formation of metal-metal bonds [3]. It has been proposed that nickel-nickel bonding is an essential characteristic of the (DMG) complex [4], and this can justify the enormous distinction in aqueous solubility of the Ni-DMG and Cu-DMG complexes, where no such bonding occurs in the latter complex; in other words, they have different crystal structures. Solubility depends on the nature of the ligand, in addition to metal-metal bond, and the influence of the ligand may be so large that it conceals the influence of the metal-metal bond [4]. Ni-DMG is more soluble than the corresponding complexes for the alicyclic vic-dioximes, which can be linked to the nature of the ligand [5]. There are other various applications of vice-dioxime such as chemical analysis [6], medicine [7], biochemistry and other fields. Vic-dioxime complexes are linked to the chemistry of vitamin B12; therefore they acquired considerable attention [8]. Some of these vic-dioximes show photo-physical and photo-chemical properties [9–12], which make them quite significant materials. Other vic-dioximes have the ability to stabilize high oxidation states of transition metals such as Cu(III) [13] and Co(IV) [14]. The stability of such species has been ascribed to the fact that the oxime group possesses some pi donor character, another factor which enhances the stability is the negative charge initiated on the oximatio-oxime. This negative charge will eventually neutralize the charge on the metal ion [13]. Different types of dioximes such as pyridine-dioxime were also reported to stabilize nickel (III, IV) [15].

This study is concerned with the coordination competence of DPG in mixed aqueous solutions.

2 Experimental

2.1 Chemicals

NaOH, KOH, NaCl, HCl, ethanol, $CuCl_2\cdot 2H_2O$, $ZnCl_2\cdot 7H_2O$ and $NiCl_2\cdot 6H_2O$ were purchased from Merck and potassium hydrogen phthalate from Fluka. All reagents were of analytical quality and were used without further purification. For the solutions, CO_2-free, double-distilled deionized water was obtained with an aquaMAX™-Ultra water purification system (Young Lin Inst.). Its resistivity was 18.2 $M\Omega\cdot cm^{-1}$.

2.2 The Synthesis of 1,2-Bis(2,6-dimethphenylamino) Glyoxime (DPG)

1,2-Bis(2,6-dimethphenylamino)glyoxime was synthesised as described in the literature [16]. To a stirred solution of anti-dichloroglyoxime 10 mmol (1.57 g) [17, 18] in absolute ethanol (30 mL), at −10 °C, was added drop-wise 20 mmol (2.42 g) of 2,6-dimethylaniline in absolute ethanol (30 mL) over a period of 1 hour. The reaction mixture was stirred for 3 hours at −10 °C. After adjusting the pH of the mixture to 5–6 with 0.1 $mol\cdot dm^{-3}$ KOH

Table 1 Summary of the experimental parameters for the potentiometric stability constant measurements

System:	DPG with H^+, Cu^{2+}, Ni^{2+} and Zn^{2+} in water
Solution composition:	$[L]/mol{\cdot}dm^{-3} = 0.001–0.002$
	$[M]/mol{\cdot}dm^{-3} = 0.001$
	ionic strength$/mol{\cdot}dm^{-3} = 0.1$ (NaCl)
Metal:Ligand ratio	1 : 2
$[NaOH]/mol{\cdot}dm^{-3} = 0.025$	
$[KHP]/mol{\cdot}kg^{-1} = 0.05$ (at 25 °C, pH = 4.005) [22]	
Volume increments/mL = 0.03	
pH range = 3–11	
$\log_{10} \beta_{00\text{-}1} = -13.98$	
$t/°C = 25.0 \pm 0.1$	
$n_{tot}{}^{a} = 230$	
$n_{tit}{}^{b} = 3$	

[a] Number of titration points per titration

[b] Number of titrations per metal:ligand system

M: metal ion, L: ligand, β: overall stability constant

solution at 0 °C, and further stirring for 1 hour and dilution with 100–120 mL of water, the reaction mixture was left overnight at 0 °C. The resulting precipitate was collected by filtration and then recrystalized from ethanol–water (1:1). The crystalline product was filtered, washed with water and dried in vacuum. Yield, 72%. Elemental Analysis: Calculated: C, 66.26; H, 6.75; N, 17.18; Found: C, 66.48; H, 6.94; N, 17.32. ^{1}H-NMR (DMSO-d_6): 10.1 (2H, s), 7.3 (2H, s), 6.6–7.1 (6H, m), 2.1–2.2 (12H, s) ppm. IR (KBr): 3390 (N–H), 3250 (O–H), 1620 (C=N), 960 (N–O) cm^{-1}.

2.3 Titration Procedure

Stock solutions (2.00×10^{-3} $mol{\cdot}dm^{-3}$) used in the titrations were prepared in aqueous solutions at 25 °C. Solutions of metals ions (0.001 $mol{\cdot}dm^{-3}$) were prepared from $CuCl_2{\cdot}2H_2O$, $ZnCl_2{\cdot}7H_2O$ and $NiCl_2{\cdot}6H_2O$ as received and standardized with ethylenediaminetetraacetic acid (EDTA) [19]. Potassium hydrogen phthalate (KHP) was prepared as buffer solution (0.05 $mol{\cdot}kg^{-1}$) and used for calibration of the combination pH electrode according to the method of Molspin [20]. NaOH (0.025 $mol{\cdot}dm^{-3}$) was standardized with primary standard KHP solution by pH-metric titration. HCl stock solutions, used for obtaining pH 3.0, were prepared from concentrated HCl and their concentration were determined with standardized NaOH. All potentiometric titrations were carried out on solutions in 100 mL double-walled glass vessel using the Molspin automatic titration system, which interfaces to a PC, with a 10 cm^3 syringe, a SenTix 20 pH combination electrode (WTW, Weilheim); the temperature was controlled at 25.0 ± 0.1 °C by circulating water from a constant-temperature bath. The cell was equipped with a magnetic stirrer and a tightly fitting cap, which contained three holes for the combined electrode, nitrogen gas and automatic burette. The pH was measured between 3.0–11.0 under nitrogen atmosphere. The ligand concentrations varied in the range $1.00–2.00 \times 10^{-4}$ $mol{\cdot}dm^{-3}$. Summaries of the titration conditions are given in Table 1. The pH-metric data was used to find the dissociation and stability constants using the SUPERQUAD computer program [21]; the standard deviations (σ values) computed by SUPERQUAD refer to random errors.

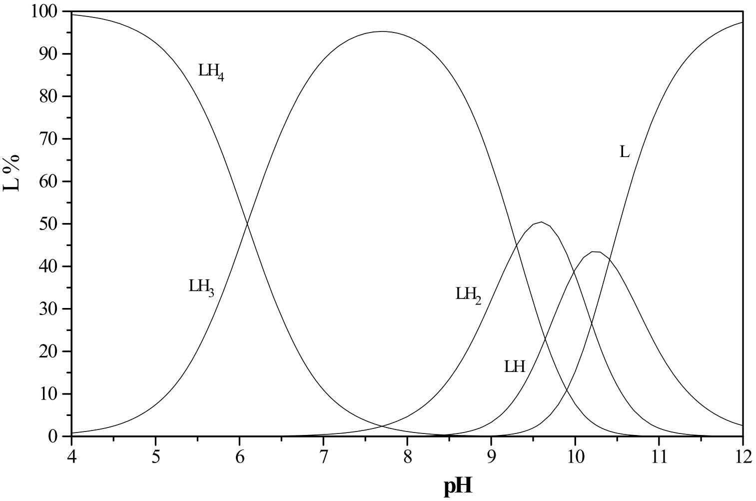

Fig. 2 Species distribution diagram of DPG, at 25 °C in aqueous NaCl ($I = 0.1\ \text{mol}\cdot\text{dm}^{-3}$)

3 Results and Discussion

3.1 Dissociation Constants of the Ligand (DPG)

The deprotonation equilibrium is as seen in the following equations (charges are omitted for simplicity).

$$\mathrm{LH}_n \rightleftharpoons \mathrm{LH}_{n-1} + \mathrm{H}$$

and the deprotonation constants (K_n) are given as;

$$K_n = [\mathrm{LH}_{n-1}][\mathrm{H}]/[\mathrm{LH}_n]$$

The distribution diagram shows that the DPG ligand exists in solution as different species depending on pH (see Fig. 2). There are four possible species that might occur under the experimental conditions. This is in accordance with the other vic-dioximes, where they expect to exhibit four pK_as as they associate to both azomehtine and hydroxyl groups (see Table 2). In the DPG ligand, the nitrogen of the imino groups is not basic enough to be determined under our experimental conditions. The four pK_as values of the DPG were determined potentiometrically (see Table 2); two of them are related to the oxime nitrogen and expressed as LH_4 and LH_3. pK_as values of DPG calculated in this study are within the expected values in comparison with other similar ligands in literature [23, 24].

It is quite useful to study the ligand forms in solution prior to the complex formation process; this will assist in predicting the possible species types which will materialize at certain conditions.

Figure 3 shows the titration curve of the DPG, together with the titration curves of dimethylglyoxime (DMG) and dichloroglyoxime (DCG) [25]. It can be noticed that the acidity extent of the DCG is comparable to DPG, as both of them differ from the DMG by replacement of a methyl group by an electron withdrawing group. DPG is even more basic than DMG, which indicates that the dimethyl phenyl amino moiety shows no electron withdrawing properties within the ligand. In other words, the dimethyl phenyl amino moiety does

Table 2 Dissociation constants of the DPG ligand with other related ligands at 25 °C in aqueous NaCl ($I = 0.100\ \text{mol}\cdot\text{dm}^{-3}$)

Ligand	Species	pK_a	Reference
DPG	LH_4	6.09 ± 0.03	Present work
	LH_3	9.30 ± 0.03	
	LH_2	9.98 ± 0.02	
	LH	10.41 ± 0.04	
BPG[a]	LH_4	2.83	[23]
	LH_3	6.06	
	LH_2	6.97	
	LH	9.51	
BBPGH2[b]	LH_4	3.46	[24]
	LH_3	5.89	
	LH_2	6.77	
	LH	9.76	
BMPG2[c]	LH_4	2.91	[24]
	LH_3	6.79	
	LH_2	7.97	
	LH	10.00	

[a] BPG: 1,2-bis(4-benzyl-piperidine)glyoxime

[b] BBPGH2: 1,2-bis(4-benzyl-piperazine)glyoxime

[c] BMPGE: 1,2-bis(4-methyl-piperazine)glyoxime

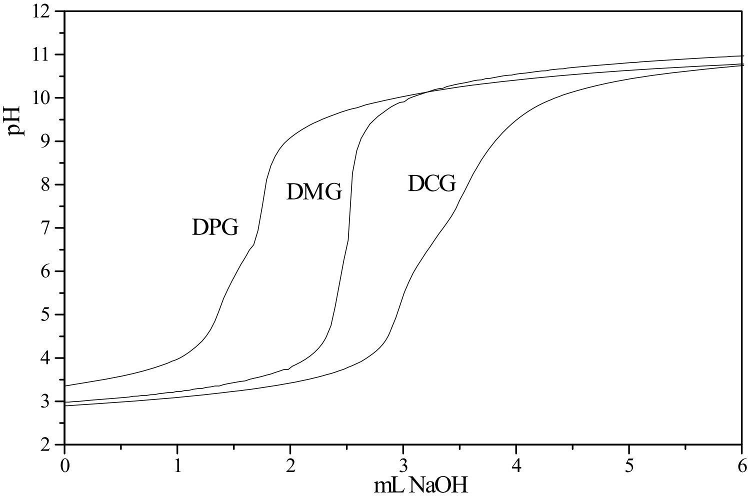

Fig. 3 Titration graph of DPG, DMG and DCG at 25 °C in aqueous NaCl ($I = 0.1\ \text{mol}\cdot\text{dm}^{-3}$)

not practically add any acidity as a result of its withdrawing properties. The high basicity of DPG, in comparison with DMG, is unexpected; again, comparing the basicity of DMG and DPG showed the diminishing electron withdrawing properties of the dimethyl phenyl group, this probably due to the electron donating properties of the methyl groups attached to phenyl ring in the molecules. This might compensate the effect of the electron withdrawing properties of the dimethyl phenyl amino group and boost the basicity of the whole DPG ligand, through pushing electron density into the whole molecule. This may be investigated by

Table 3 Stability constant data for the complexation of Cu^{2+}, Ni^{2+} and Zn^{2+} with DPG at 25 °C in aqueous NaCl ($I = 0.1\ \text{mol}\cdot\text{dm}^{-3}$) $\beta_{pqr} = [M_pL_qH_r]/[M]^p[L]^q[H]^r$

	pqr[a]	Ni(II) $\log_{10}\beta_{pqr}$	Cu(II)	Zn(II)
M(II)-DPG complexes	101	18.41 ± 0.06	17.15 ± 0.05	18.05 ± 0.02
	111	27.66 ± 0.07	25.90 ± 0.02	26.47 ± 0.02
	121	36.73 ± 0.04	32.37 ± 0.05	–
	131	45.38 ± 0.04	38.83 ± 0.03	41.72 ± 0.02
	141	51.41 ± 0.05	42.92 ± 0.04	47.94 ± 0.03
	1–11	–	7.50 ± 0.04	–
	1–21	−0.63 ± 0.04	−2.17 ± 0.04	−0.34 ± 0.02
	1–31	−10.75 ± 0.08	−12.04 ± 0.05	–
	1–41	–	–	−19.99 ± 0.04

[a] p: number of metal ions, q: number of hydrogen ions (positive values) or hydroxide ions (negative values), r: number of ligands, in the complexes

using other similar ligands with no donating groups. The higher basicity of DPG in comparison to DMG lessens the dissociation of the hydroxyl groups in the molecule. But, during the coordination of the ligand with the metal ion, this process enhances the dissociation of the hydroxyl group resulting in the generation of hydrolyzed species (see Table 3) and proton release.

3.2 Stability Constants of the Complexes

The overall stability constants (β_{pqr}) are defined as follows (charges are omitted for simplicity):

$$pM + qL + rH \rightleftharpoons M_pL_qH_r, \qquad \beta_{pqr} = [M_pL_qH_r]/[M]^p[L]^q[H]^r$$

where M is a metal ion, L is the ligand, H is the proton, and p, q and r are the respective stoichiometric coefficients.

Figure 4 shows the titration curve of the M-DPG complex system. As seen in Fig. 3, the inflection points are different for each metal ion, M.

The bi-dentate nature of the DPG ligand imposes a cis-structure of the coordinated ligand; this makes clear the extent of the coordinating power of the ligand and indicates its affinity towards metal ions. Thus the trans-form the DPG cannot act as a bi-dentate ligand, yet has less steric strain. The cis form can also be found in one of the following structures, syn(α), anti(β) and amphi(γ) [26]. The anti form seems to be the most appropriate structure for coordination with metal ions.

Generally the main mode of coordination of vice-dioximes with the transition metals takes a square planar geometry through the two nitrogen atoms in the oxime chain [9, 27–29], leading to a five membered ring chelate. Other, six membered ring chelates may also be formed [30] but to a lesser extent. Coordination in this manner enhances the dissociation of the hydroxyl groups, and this assists the formation of symmetrical intra-hydrogen bonding in the case of bis-vic-dioxime complexes [31]. Vic-dioximes also form complexes with structures other than square planar [32].

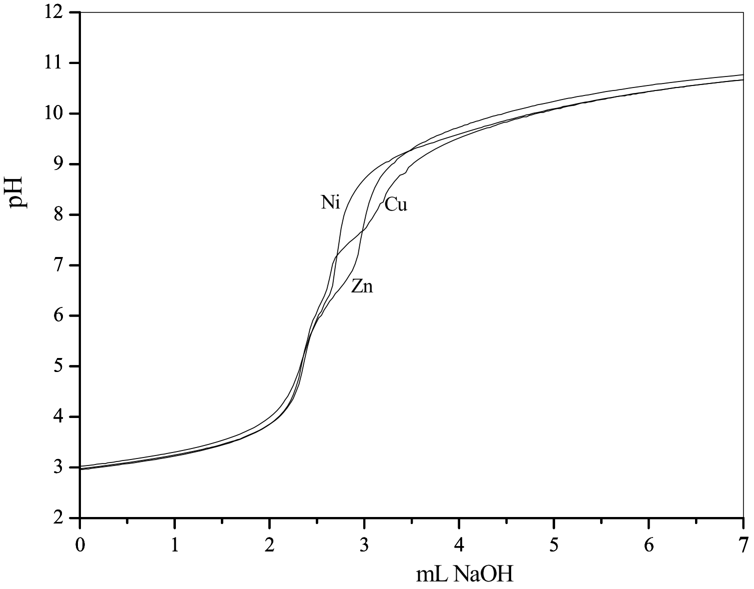

Fig. 4 Titration graph for M-DPG at 25 °C in aqueous NaCl ($I = 0.1\ \text{mol}\cdot\text{dm}^{-3}$)

The ligand DPG forms only mono binary complexes in solution despite the experimental conditions potentially allowing formation of a bis-complex. The immense size and the structure of the ligand might be the primary factor preventing formation of the bis-complex. The relatively large DPG molecule will occupy more space of the inner coordination sphere, leaving insufficient room for a second molecule of the ligand to be attached. The structural shape of the DPG ligand imposes strain on coordination, as the two 2,6-dimethyl amino moieties are situated nearby within the molecule, where there is a possible contact between them which eventually affects the coordination.

The relative high stability constants of the main complexes in all metal ion used in this research (see Table 3) indicate that steric hindrance has less influence than expected. This may be explained on the basis that the DPG ligand is capable of adapting its shape as it approaches a metal ion, where it keeps the steric hindrance at its minimal.

Intra-complex hydrogen bonding would not be possible, but inter-molecular hydrogen bonding is quite likely; this would be encouraged by the increased acidity of the hydroxyl group upon coordination. This type of hydrogen bonding increases the solubility of the complex in solution.

For the Ni-DPG system, the complex formation spans between pH = 4 to pH = 12, and a variety of species are traced (see Fig. 5). At the early stages and up to pH 8.75 NiH_4L and NiH_3L are almost the only species present. NiH_4L decreases at approximately pH = 7; while NiH_3L can be found in solution up to almost pH = 9. The NiH_2L species can be found in solution in basic medium and starts to develop in significant amounts just above pH = 8, and at pH = 8.75 it forms about 40% of the total metal ion concentration. At the same pH (8.75) and up to pH = 9.25, NiHL developed too but to a lesser extent, forming less than 30%. NiL species occurred at slightly higher pH than NiHL. So the species which can be traced between pH 8.75–9.00 are: $NiLH_3$, $NiLH_2$, NiLH, and NiL. After pH = 9 and up to pH just above 11, two more hydrolyzed species come into solution and they are $NiLH_{-2}$ and NiH_{-3}, and above pH = 11 only the species $NiLH_{-3}$ exists.

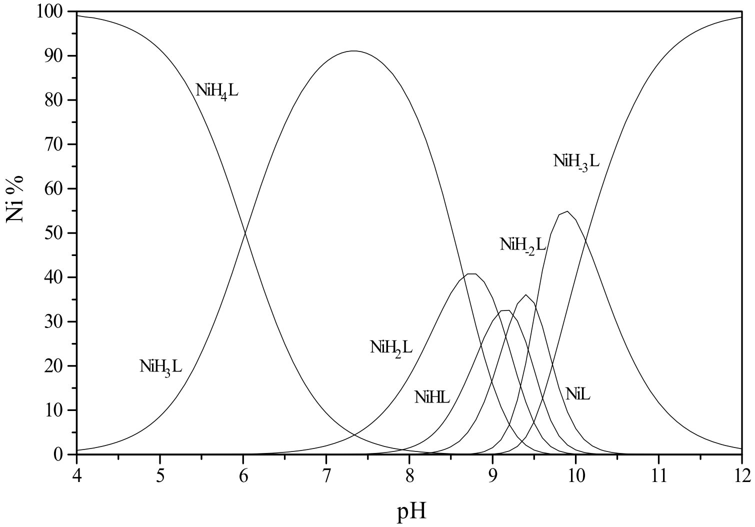

Fig. 5 Species distribution diagram for the Ni-DPG system, at 25 °C in aqueous NaCl ($I = 0.1$ mol·dm^{-3})

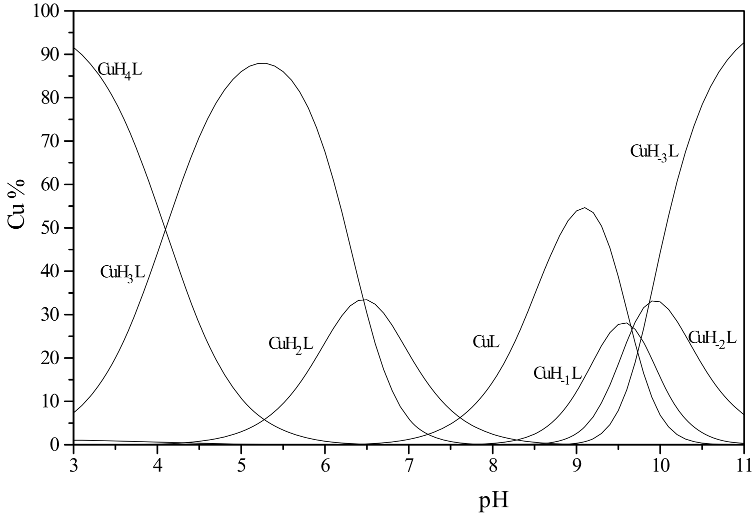

Fig. 6 Species distribution diagram for the Cu-DPG system, at 25 °C in aqueous NaCl ($I = 0$ mol·dm^{-3})

It is expected that the distribution curve in the case of the Cu-DPG system would be similar to that of the Ni-DPG system. Figure 5 shows the resemblance between the two systems, but different species in the case of Cu-DPG formed at relatively lower pH than the Ni-DPG system. This is expected, as Cu(II) in aqueous solution is more acidic than the corresponding Ni(II) [33]; however, this actually doesn't necessitate higher stability of Cu-complexes over the Ni-complexes. Figure 6 also shows that the Cu-species span over a wider pH range than the Ni-species, especially in the acidic region.

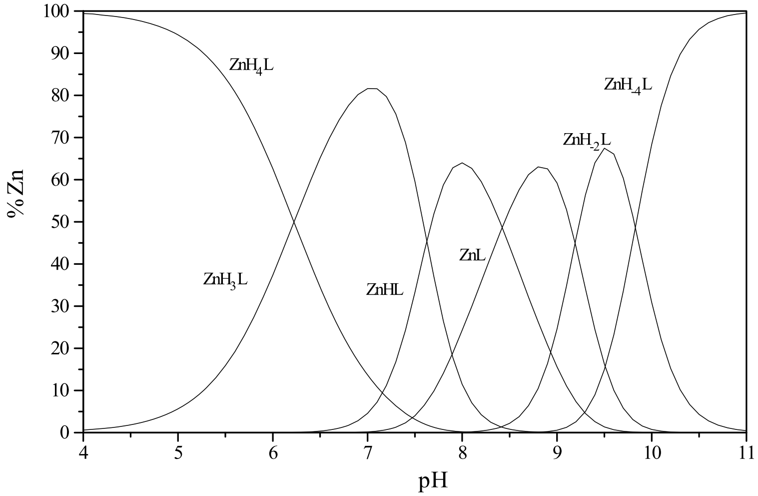

Fig. 7 Species distribution diagram for the Zn-DPG system, $I = 0.1\ \text{mol}\cdot\text{dm}^{-3}$ NaCl, at 25 °C

Cu-DPG species formed in solution over a wide range of pH values (3–11+), where at lower pH (3–5) only CuLH_4 and CuLH_3 are formed and dominate the solution. At pH exceeding 5, the complex CuLH_2 starts to form and within the range of pH = 5–9, and in addition to the above species, the complex CuL forms reaching a maximum of 55% of the total metal ion at pH = 9.

The hydrolyzed species CuLH_{-1} and CuLH_{-2} and formed in solution between pH = 9.5 and 10 with about 30% of each. At pH higher than 10.5, CuLH_{-3} will be the dominant species in the solution.

Considering Fig. 7, which shows the distribution diagram of the Zn-DPG system, different species are formed at wide pH range too. Species are formed at almost the same pH as in the Ni-DPG system, but higher than for Cu-DPG. This again reflects the acidity of the partially complexed ion.

Zn-DPG species formed in solution over a wide range of pH (4–11); at pH (4–5), the only species present in solution is ZnLH_4 with a maximum percentage above 95% of the total concentration of the metal ion at pH = 4. The species ZnLH_3 starts to form just above pH = 5 and reaches its maximum percentage of 80% of the metal ion at pH = 7. Above pH = 7 and up to pH = 9 the main species in the solution are the ZnHL with a maximum percentage of 62% at pH = 8, and the other species is ZnL with a maximum percentage of 60% at pH = 8.8. The other two hydrolyzed species ZnLH_{-2} and ZnLH_{-4} are formed in the solution at pH range 8.75–11 with maxima of 65% at pH = 9.5 and more than 95% at pH above 11 respectively.

Hydrolyzed species occur as a result of the dissociation of the hydroxyl groups of the ligand and/or hydrolysis of water molecules in the coordination sphere of the complexed ion. The partially coordinated metal ion in aqueous solution would undergo hydrolysis at pH less than for the aquated ion, as the coordination between the ligand and the metal ion in solution will influence the water molecules coordinated to the ion, whereby it eventually facilitates hydrolysis. At the high pH applied in this work, it is highly expected that such a process would take place; as the pK of Ni(II) is about 7.6 [33].

The mixed solvent affects the dissociation of the aquated metal ion, raising the dissociation constant [34]. On the other hand, the relatively big size of the ligand may influence the coordinated water molecules resulting in weakening of the coordination with the metal ion. This may further decrease the hydrolysis of the aquated metal ion in the binary complex. The process of hydrolysis of the aquated binary metal complex, which entails the dissociation of a proton from one or more of the water molecules, takes place at a relatively higher pH than hydrolysis of the aquated metal ion $[M(H_2O)_6]^{2+}$ (M is Ni, Cu, or Zn). This is due to the decrease of the coordination power of the metal ion as a result of partial neutralization by coordination with the molecule.

On the other hand, the hydrolyzed species may be accounted for by the dissociation of hydroxyl groups in the ligand. The pK_as of the hydroxyl groups are 9.98 and 10.41 respectively (see Table 2) and these values suggest that the hydrolysis can occur as a result of the hydroxyl groups dissociation. But, it is hard to judge exactly the source of the hydrolyzed species in solution; it may be a result of the both processes, each contributing to a different degree.

So the possibility exists for the formation of hydrolyzed species under our experimental conditions, by one or both of these processes. The hydrolysis process is influenced by pH, the strength of coordination bonding between metal ion and the ligand, and the availability of water molecules on the complexed ion.

The order of the stability of the complexes under investigation is Ni > Zn > Cu (Table 3) which contravenes to Irving-William series [34]. The outstanding stability of the nickel complex over that of copper can be explained in terms of the possible linkage between nickel-nickel ions in the solution [35]. This type of linkage can not be considered as proper bonding as in the case of solid complexes [35]. Still it has its own impact on coordination, despite that there is no trace of poly-nuclear complexes recorded under our experimental conditions. This is due to the low concentration of such complexes, which makes them undetectable by means of the computer program.

All Zn-DPG complexes formed in solution are more stable than the corresponding Cu-DPG complexes; this is again not expected on the light of Irving William order [34]. This can be explained in terms of the possible existence of aquated Zn-DPG complexes in the form of a tetrahedral arrangement with a $[Zn\text{-}(DPG)(H_2O)_2]^{2+}$ structure. So the additional stability initiated was through the entropy factor, which was raised by the loss of more water molecules from the aquated zinc ion through coordination.

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