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THE AFFINITY OF SOME AMINOMETHYLENE POLYPHOSPHONIC ACIDS TOWARDS Cu(II), Ni(II), Co(II), Zn(II) in SOLVENT–MIXTURES[*]

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BAZI AMİNOMETİLEN POLİFOSFONİK ASİTLERİN ÇÖZÜCÜ KARIŞIMLARINDA Cu(II), Ni(II), Zn(II) İYONLARINA KARŞI AFFİNİTESİ

ÖZET

Geniş endüstriyel kullanım alanlarına sahip olan nitrilometilen trifosfonik asit (NTMP), metil iminodimetilen difosfonik asit (MIDMPA) ve monoetanolamin dimetilen difosfonik asit (MEADMPA) izole edildi ve bazı analitik özellikleri incelendi. Protonlanma basamakları ve bazı analitik özellikleri tayin edildi. Dielektrik sabiti yaklaşık 59 olan su ve organik çözücü ortamlarında (dioksan, aseton, metanol, etanol), ve farklı dielektrik sabitlerine sahip isopropanol/su çözeltilerinde (56; 62,90; 69,40; 74,40) ve 25 ± 0,5 °C'de Cu(II), Ni(II), Co(II) ve Zn(II) iyonlarıyla elde edilen 1/1 komplekslerin protonlanma basamakları ve analitik stabilite sabitleri tespit edildi. Organik çözücü varlığında kompleks stabilitelerinin sulu çözeltilere nazaran genel bir artış gösterdiği bulundu.

SUMMARY

Nitrilotrimethylene triphosphonic acid (NTMP), methyl iminodimethylene diphosphonic acid (MIDMPA), and monoethanolamine dimethylene diphosphonic acid (MEADMPA) which have wide industrial uses were isolated and some analytical properties were investigated. The protonation step values and analytical stability constants of 1/1 complexes of the ligands with Cu(II), Ni(II), Co(II), Zn(II) were determined at 25 ± 0.5 °C. The same dielectrical constant ($\approx$ 59) was adjusted in aqueous and organic solvent media (dioxane, acetone, methanol, ethanol) whereas isopropanol/water solutions had different dielectrical constants (56, 62.90, 69.40, 74.40). It was found that in the presence of an organic solvent, a general increase in complex stabilities were observed compared to aqueous solutions.

1. INTRODUCTION

Some of amino–polyphosphonates are used as scalant formation preventer in reaction vessels since they have been known as anti-crystal growth agents [1] and they have an excellent metal–capturing property [2, 3].They function as a corrosion inhibitor by forming a protective film in the systems in which water–cooling processes are carried on. In addition, these compounds have versatile applications ranging from industrial detergents to home cleaners and are stable to hydrolysis [4]. They can be used within wide pH and temperature ranges, and because of the *threshold* effect[**]; they are more superior than

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[**] the prevention of precipitation from supersaturated solutions of scalants

inorganic polyphosphates. Among these compounds studied, NTMP has the least toxicologic effect and the most important one of aminomethylene polyphosphonic acids in which the chelating properties in aqueous solutions (M/L: 1/1) were investigated regarding the effect to the environment [5].

Nitrilotrimethylene triphosphonic acid (NTMP, H_6L^1), monoethanolamine–dimethylenediphosphonic acid (MEADMPA, H_5L^2) and methylimino–dimethylene diphosphonic acid (MIDMPA, H_4L^3) are from the sub–group of aminomethylene polyphosphonic acids which are a main group of aminoalkane phosphonic acids. In our study, the protonation steps and affinities towards Cu(II), Ni(II), Co(II) and Zn(II) ions of the polybasic ligands were investigated in different solvent-mixtures. The analytical stabilities of the metal complexes with 1/1 M/L ratio were calculated by means of *pKas* computer program [6].

2. EXPERIMENTAL SECTION

2.1 Preparation of the ligands

The ligands were prepared with small modifications of general methods based on *Mannich*–type reactions, and yields were slightly improved [7, 8, 9, 10]. When the reaction was carried out at low pH values, optimum results were obtained. In addition, the yields of these reactions were increased by using mercury gas traps in an isolated system. Melting points (°C), recrystallization solvents and yields (%) for $H_{6-4}L^{1-3}$ are given respectively as follows: 210–215 (decom.), glacial acetic acid, 82; 210 (decom.), metanol/ethanol (1:1), 70; 255 (decom.), methanol, 68.

The ligands were characterized by elementel analysis and by their melting points. Their purity were checked by TLC.
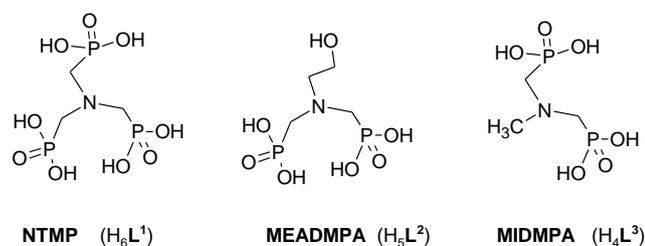

NTMP (H_6L^1) **MEADMPA** (H_5L^2) **MIDMPA** (H_4L^3)

Figure 1. Structures of the ligands.

2.2 Potentiometric titrations

A digital pH–meter, AG EA 121 standard glassware electrode and a burette equipped with a piston were used. Dielectrical constant measurements were done in $25 \pm 0.5°C$ with an MF_3 cell by a DK06 model multidecameter (Frequency=1.3 mc/sec). All the chemicals used were of analytical reagent grade.

As the solvent media for titration, water and several organic solvents including dioxane–water (30.80%, w/w), methanol–water (45.30%, w/w), ethanol–water (32.50%, w/w), and acetone–water (35.50%, w/w) which have nearly the same dielectrical

constant (D=59) were preferred. In addition to this series of solvent-mixtures with the same dielectrical constant, studies were also focused on varying the dielectrical constant by changing the composition of the isopropanol–water solution as follows: 10% v/v, D= 75.4; 20% v/v, D= 70.4; 30% v/v, D= 64; and 40% v/v, D=59. The concentration (mol/L) of L^{1-3} (T^0_L), $HClO_4$ (E^0), $NaClO_4$, metal salts (T^0_M) and NaOH (N) are $5 \cdot 10^{-2}$, 0.25, 0.1 and 0.5, respectively. These solutions were used to prepare the starting mixtures according to the Irwing–Rossotti's technique [11, 12], in which the total volume is constant in all mixtures. The composition of each mixture is given below.

a: 5 mL $HClO_4$ + 5 mL $NaClO_4$ + 30 mL solvent.
b: 5 mL $HClO_4$ + 5 mL $NaClO_4$ + x mL ligand + (40–10–x) mL solvent; x=2, 4, 8, 12 and 16 mL.
c: 5 mL $HClO_4$ + 5 mL $NaClO_4$ + 12 mL ligand + 6 mL metal chloride + 12 mL solvent.

A series of potentiometric titrations of a, b and c were carried out by using each solvent media mentioned above at $25 \pm 0.5\,^{\circ}C$.

3. RESULTS AND DISCUSSION

3.1 Protonation constants of the ligands

At the optimum concentration of the ligand (1.5×10^{-2} M), the probable number of protonation steps (j) and protonation values (β) of H_6L^1, H_5L^2 and H_4L^3 were included in Table I. These parameters were determined via $n'_A = f(pH)$ curves (Figure 2).

The protonation constants corresponding to β_5 and β_6 for H_6L^1, β_5 for H_5L^2, β_4 for H_4L^3 could not be determined. In an aqueous solution of H_6L^1 and the concentration range studied, the first proton (and the second proton in H_6L^1) has already dissociated, and thus, the steps could not be found in $\tilde{n}_A = f(pH)$ curve. Therefore, extrapolation had to be done to obtain these β values of the ligands. The values of β_5 and β_6 for H_6L^1 (See Table I) were found to be suitable to the values given in the literature [13]. In fact, in the earlier investigations, it was seen that these values could be given as ≤ 2 and ≤ 1 [3].
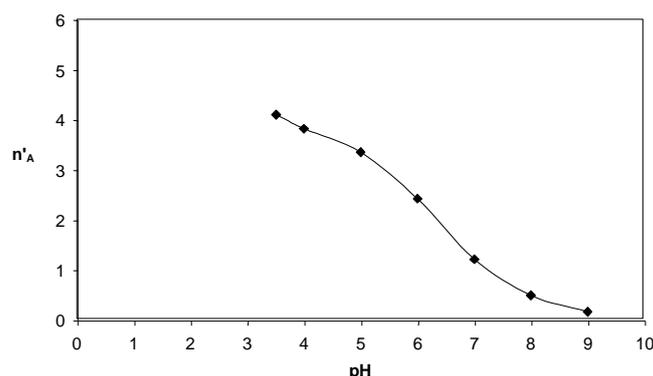

Figure 2. Protanation steps of H_6L^1 in ethanol (w%, 34,50; D=58,50)

H_6L^1 exists as dipolar species in solution and while it is in zwitterionic form, $[NH^+(CH_2P(O)(OH)_2)_2(CH_2P(O)(OH)O)^-]$, the first step value ($\beta_1$) is significantly higher

than the others, indicating that the first proton entrance occurs through the nitrogen atom (Table II).

The determination of protonation steps in different solvent-mixtures with nearly the same dielectrical constant yielded similar results, whereas the results with acetone were different. It is obvious that in the solutions prepared with acetone, especially β_{1-4} values are greater, with comparison to the other organic solvent-mixtures.

As the dielectrical constant of the isopropanol-water mixture decreases, the protonation constants of H_6L^1 decrease, too. Therefore, it was observed in our study that protonated species dissociate with more difficulty in the organic solvent–containing mixtures and, in contrast, dissociation becomes easier in solvents with lower dielectrical constants (Table I). According to that, the equilibrium

$$L^{n-} + H^+ \rightleftharpoons LH^{(n-1)-}$$
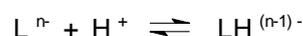
shifts to left as the polarity of the solvent decreases. The mentioned tendency results from the lower solubilities of polyphosphonic acid in the organic solvent medium.

3.2 Analytical stability constants of the complexes

Analytical stability constants (K_n) of H_6L^1 with Cu(II), Ni(II), Co(II) and Zn(II) ions [14, 15] (Table III) that were reported with 1/1 metal/ligand ratio were calculated by the equation, $K = 10^{-pL}$, which was found after finding the pL values from the half integral values (0.5, 1.0, etc) of the formation function from the ñ= f(pL) curve (Figure 3).
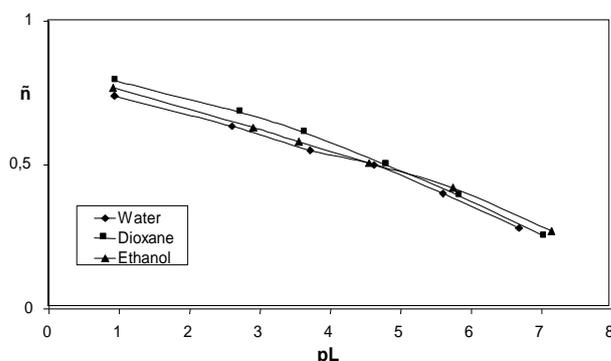

Figure 3. Formation curves of H_6L^1-NiCl$_2$ complexes (1:1) in different solvent-mixtures.

There is only one complexation step of the ligands with Cu(II), Ni(II), Co(II) and Zn(II) ions in which coordination occurs between equivalent amounts of metal and ligand[3], such as NTA or EDTA. In the organic solvent-mixtures which have a dielectrical constant value of approx. 59, there is not any considerable difference in the stabilities of the metal complexes. In a similar manner, it was observed that log K values of Cu(II) complexes with H_6L^1 in water/isopropanol mixture were not significantly different as the dielectrical constant of the solution decreases (D, log K: 74.40, 2.82; 69.82, 2.72; 62.90, 2.65; 56.05, 2.62). It is apparent that solvent molecules do not affect the complexation equilibrium of metal cations coordinatively or by any other means. However, the stabilities yield an obvious increase in the presence of organic solvents.

Here, the most positive effect is observed with acetone. As a consequence of the lower solubility of the ligand, the observed increase is worth noticing. The log K value which is 2.92 for Cu(II)$-$H$_6$**L**^{1} in water is 4.05 in acetone–water mixture. This result which can be due to the source of the higher solubility of the metal complex in mixed solvents rather than the free ligand shows that H$_6$**L**^{1} can be used as an extraction agent in organic solvent medium.

Table 1. The log β_n values of H$_6$**L**^{1}, H$_4$**L**^{2} and H$_5$**L**^{3} in different solvent-mixtures ([*]).

Solvent (%w) in mixture	D [**]	H$_6$**L**^{1} (NTMP)					
		Log β_1	Log β_2	Log β_3	Log β_4	Log β_5 [***]	Log β_6 [***]
Water, 100	78.40	11.75	7.40	5.85	4.65	2.05	0.80
Dioxane, 30.80	58.25	8.95	7.00	6.15	4.70	2.10	1.05
Acetone, 35.50	58.76	10.40	7.55	6.50	5.35	1.90	0.95
Methanol, 45.30	58.95	8.15	7.10	6.15	4.85	2.30	1.10
Ethanol, 34.50	58.50	8.05	6.65	5.90	4.75	2.15	1.00

Solvent (%w) in mixture	D [**]	H$_5$**L**^{2} (MEADMPA)				
		Log β_1	Log β_2	Log β_3	Log β_4	Log β_5 [***]
Water, 100	78.40	12.70	10.95	7.35	5.05	0.75
Methanol, 45.40	58.95	12.40	10.00	7.25	5.05	0.65
Ethanol, 32.50	58.50	12.25	9.75	7.05	5.00	0.60

Solvent (%w) in mixture	D [**]	H$_4$**L**^{3} (MIDMPA)			
		Log β_1	Log β_2	Log β_3	Log β_4 [***]
Water, 100	78.40	11.00	6.15	5.05	1.10
Methanol, 45.30	58.95	11.20	6.60	5.35	1.55
Ethanol, 32.50	58.50	11.05	6.50	5.25	1.05

([*]) *Determinations were carried out at 1M NaClO$_4$ ionic strengths and 25$\pm$0.5 ^{o}C.*
([**]) *measured values.*
([***]) *found by extrapolation within the error range $\pm$0.05.*

The effect of ligand's solubility to complex stability can easily be seen by investigating the structures. The solubility of H$_4$**L**^{3} is less in organic media because it has two less phosphonate groups compared to H$_6$**L**^{1}.

It will be noticed in Table III that the stabilities of complexes with H$_5$**L**^{2} are higher than those of the other two. It can be said that the structure of H$_5$**L**^{2} is different according to the others at this pH value. Therefore, H$_5$**L**^{2} should be excluded in the comparison and considered individually.

By taking the results into account, it has been applied to metal−capturing ability of the aminomethylene phosphonic acids towards first row−transition metal ions. Henceforth, using the ligands in media containing organic solvents for various purposes will probably cause its utility in several applications.

Table 2. The Log β_n values of H_6L^1 in water/isopropanol mixtures (*).

Isopropanol (v%) in the mixture	**10**	**20**	**30**	**40**
D (*measured*)	74.40	69.82	62.90	56.05
log β_1	9.40	7.80	7.80	7.70
log β_2	6.80	6.65	6.60	6.50
log β_3	5.80	5.65	5.60	5.65
log β_4	4.55	4.45	4.40	4.25
log β_5	1.90	1.70	1.55	1.50
log β_6	0.70	0.60	0.55	0.50

(*) (1M $NaClO_4$, 25 ± 0.5^oC).

Table 3. The analytical stability constants of $H_{6-4}L^{1-3}$ complexes with Cu(II), Ni(II), Co(II), Zn(II) (*).

Solvent (%w) in mixture	Ligand	$D^{(**)}$	Analytical Stability Constants, log K			
			Cu(II)	**Ni (II)**	**Co(II)**	**Zn(II)**
Water, 100		78.40	2.92	4.60	3.37	3.35
Dioxane, 30.80	H_6L^1	58.25	3.65	4.80	4.10	3.92
Acetone, 35.50	(NTMP)	58.76	4.05	4.90	4.20	4.27
Methanol, 45.30		58.95	3.77	4.80	4.35	4.40
Ethanol, 32.50		58.50	3.50	4.55	4.52	4.90
Water, 100	H_5L^2	78.40	7.20	7.94	7.56	7.42
Methanol, 45.30	(MEADMPA)	58.95	6.60	7.95	7.90	8.22
Ethanol, 32.50		58.50	7.63	7.77	7.80	8.10
Water, 100	H_4L^3	78.40	1.77	3.05	2.48	2.31
Methanol, 45.30	(MIDMPA)	58.95	1.85	2.90	2.40	2.70
Ethanol, 32.50		58.50	1.88	3.12	2.55	2.52

(*)$1.5 \ 10^{-2}$ M concentration (1 M $NaClO_4$, $25\pm0.5°C$).

(**) measured values.

REFERENCES

[1] MARK F.K., KETTA J.J., OTHMER I.D., "Kirk-Othmer Encyclopedia of Chemical Technology", Second Edition, 15, 320-330, 1968.

[2] SAWADA K., ARAKI T., SUZUKI T., "Complex Formation of Amino Polyphosphonates. 1. Potentiometric and Nuclear Magnetic Resonance Studies of Nitrilotris(methylenephosphonato) Complexes of the Alkaline Earth Metal Ions", J. Inorg. Chem., 26, 1199-1204, 1987.

[3] SAWADA K., ARAKI T., SUZUKI T., "Complex Formation of Amino Polyphosphonates. 2. Stability and Structure of Nitrilotris(methylenephosphonato) Complexes of the Divalent Transition Metal Ions in Aqueous Solution", J. Inorg. Chem., 28, 2687-2688, 1989.

[4] MAIER L., "Organophosphorus Detergents", Chimia, 23, 323-330, 1969.

[5] STEBER J., WIERICH P., "Properties of Aminotris (methylenephonate) Affecting its Environmental Fate", Henkel–Referate, 24/int.Ed.,76-82, 1988.

[6] MARTELL A.E., MOTEKUITIS R.J., "Determination and use of stability constants", second edition, VCH Publishers, Inc., 1992.

[7] MOEDRITZER K., IRANI R.R., "The Direct Synthesis of α-Amino-methylphosphonic Acids. Mannich-Type Reactions with Orthophosphorous Acid", J. Org. Chem., 31, 1603-1607, 1966.

[8] CHAMBERS J.R., ISBELL A.F., "A New Synthesis of Amino Phosphonic Acids", J. Org. Chem., 29, 832-836, 1964.

[9] KRÜGER F.V., BAUER L., "Ein Neues Verfahren zur Darstellung von Aminomethylenphosphonsäuren", Chemiker-Zeitung, 96, 12, 691, 1972.

[10] WESTERBACK S., RAJAN K.S., MARTELL E.A., "New Multidentate Ligands. III. Amino Acids Containing Methylenephosphonate Groups", J. Am. Chem. Soc., 87:12, 2567-2572, 1965.

[11] IRWING H.M., ROSSOTTI S.H., "The Calculation of Formation Curves of Metal Complexes from pH Titration Curves in Mixed Solvents", J. Chem. Soc., 2904-2910, 1954.

[12] ROSSOTTI F.J.C., ROSSOTTI H., "The Determination of Stability Constants", McGraw-Hill Book Company, Inc., New York, 391-410, 1961.

[13] SAWADA K., KURIBAYASHI M., MIYAMATO H., "Protonation Equilibria of Nitrilotris (methylenephosphonato) and Ethylenediamine tetrakis(methylenephosphonato) Complexes of Scandium, Yttrium and Lanthanoids", J. Solution Chem., 20, 829-839, 1991.

[14] HENDRICKSON S.H., "Comparison of the Metal-Binding Properties of Nitrilotri(methylenephosphonic) acid and Nitrilotriacetic acid: Calcium(II), Nickel(II), Iron(III), and Thorium(IV) Complexes", Anal. Chem., 39, 2, 998-1000, 1967.

[15] CARTER R.P., CARROL R.L., IRANI R.R., "Nitrilotri(methylene phosphonic Acid), Ethylimino(methylene phosphonic acid), and Diethylaminomethylphosphonic Acid, Acidity and Calcium (II) and Magnesium (II) Complexing", Inorg. Chem., 6, 939-942, 1967.

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