

**Stability of Metal Chelates of 2-Sulphonic-4-Methyl
Phenylhydrazono Diethylmalonate in
Various mixed Aqueous Solvents**

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Summary: pH-metric studies have been carried out to determine the dissociation constant of 2-Sulphonic-4-methyl phenyl-hydrazono di-ethylmalonate abbreviated (2-SPHDEM) ligand, as well as, the stability constants of its complexes with trivalent lanthanides and some divalent metal ions in various mixed aqueous solvents, viz: ethanol-water, methanol-water and dioxane-water at 25°C and 0.1 M ionic strength. The dissociation constant of ligand decreases (increase in acidity) by increasing the dielectric constant of the solvent. The stability constants of 1:1 and 1:2 chelates with trivalent lanthanides have been determined in 50% (v/v) ethanol-water solvent. The effect of variation of the dielectric constant of different mixed aqueous solvents on the stability of chelate compounds of divalent metal ions was studied and discussed. The stability of these chelates follows the order: dioxane-water > ethanol-water > methanol-water.

In an ethanol-water mixture, the sequence stability is:
75% > 50% > 25% > 0.0%

The stability constants of divalent metal ions in all solvents studied follows the order:

$\text{Cu(II)} > \text{Zn(II)} > \text{Ni(II)} > \text{Co(II)} > \text{Cd(II)}$.

Introduction

The nature of solvent and its mole fraction play an important role on the value of dissociation constant of many organic ligands [1,2,3] as well as the stability constants of chelate compounds [4,5]. Recently the effect of solvent on the dissociation constant of *o*-carboxyphenyl hydrazo-ethyl-acetoacetate ligand and the stability constant of its chelate compounds with some bivalent transition metals have been reported [6].

In the present communication pH-metric titration has been used to determine the acid dissociation constant of 2-sulphonic-4-methylphenyl hydrazonodiethylmalonate ligand and the consecutive stability constants of its complexes with trivalent lanthanides and bivalent transition metals. The solvent effect on pK_a of the studied ligand as well as, the stability constants of its chelate compounds with

Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) has been investigated.

Experimental

a) Preparation of organic ligand

The ligand 2-SPHDEM was prepared by coupling the diazonium salt of 2-sulphonic-4-methyl aniline with diethylmalonate in presence of sodium acetate [7]. The pure product was obtained after several crystallization from ethyl alcohol. The purity of the organic ligand was examined by infrared spectra and elemental analysis: Found C, 44.43; H, 4.41; N, 8.28 calculated for $C_{14}H_{17}O_7N_2SNa$: C, 44.20; H, 4.47; N, 8.42. The free ligand is easily soluble in water since it is present as the sodium salt which decomposed before melting at high temperature.

b) Solutions

Stock solutions of lanthanide nitrate were prepared as described previously [8]. Solutions of Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) were prepared from their nitrates and standardization by the recommended method. The titration of Lanthanide-2-SPHDEM were carried out in 50% (v/v) ethanol-water mixture. The titration of 2-SPHDEM in absence and in presence of divalent metal ions were performed in 0.0%, 25%, 50%, 75% ethanol-water; 50% methanol-water and 50% dioxane-water solvents. The ionic strength was maintained constant at 0.1M by the addition of potassium nitrate. All the measurements were carried out in inert atmosphere by bubbling oxygen free nitrogen gas through the solutions. The metal : ligand ratio was maintained at 1:2 and 1:3 for bivalent transition metal and trivalent lanthanide respectively. The solutions were titrated against 0.1M potassium hydroxide solution in the proper solvent. Corrections for change in volume which took

place during the course of titration were made in all cases studied. The pH readings were corrected in dioxane-water [9], ethanol-water and methanol-water solvents. All the chemicals used in this study were of the BDH type.

c. Apparatus

The pH-meter used in this study was WTW type with combined electrode. The infrared spectrum was recorded in the solid state on a Perkin-Elmer Model 437 spectrometer from 200-4000 cm^{-1} using KBr disc technique.

Results and Discussion

(1) Dissociation constant of 2-SPHDEM in mixed aqueous solvents

The titration of 50 ml of the free ligand was carried out in 0.0%, 25% and 75% (v/v) ethanol-water as well as in 50% (ethanol-water) and in 50% (methanol-water) and (dioxane-water) solvents at 25° and 0.1 M strength. The calculated pK_a values in different solvents are recorded in Table-1.

The variation of pK_a with concentration of organic solvent in the mixture (Table-1) suggests that the acid dissociation constants (K_a) decreased with increase in % ethanol, methanol and dioxane in the mixture. This is in agreement with the expectation that the ionization of the acid should decrease with the decrease in the dielectric constant (ϵ) of the solvent as observed with other acids [6,10]. In 50% (v/v) mixed solvent, the sequence of $1/\epsilon$ in different mixed aqueous solvents is: dioxane-water ethanol-water > methanol-water. The pK_a values in the three mixed solvents are in the order dioxane-water ethanol-water > methanol-water. For

Table-1: pK_a values for 2-SPHDEM in various mixed aqueous solvents at 25° and 0.1M ionic strength.

Solvent composition % (v/v)	$1/\epsilon$	pK_a
0.0 % Ethanol-water	0.0130	10.01 ± 0.02
25 % Ethanol-water	0.0151	10.29 ± 0.05
50 % Ethanol-water	0.0194	10.42 ± 0.03
75 % Ethanol-water	0.0271	10.94 ± 0.05
50 % Methanol-water	0.0178	10.20 ± 0.04
50 % Dioxane-water	0.0293	11.83 ± 0.03

particular solvent, e.g. ethanol-water, the pK_a values of the ligand increase by increasing the % of ethanol. The sequence in ethanol-water mixture is: 75% ethanol-water > 50% ethanol-water > 25% ethanol-water.

Furthermore, these results can be explained on the basis that an intramolecular hydrogen bonding between the carbonyl groups of the ester branch and the hydrogen of the hydrazo group may be formed [6]. The tendency to form hydrogen bond is greatly affected by increasing the percentage of hydroxyl solvent (i.e., % of water). Thus increasing the % of water in the solvent would decrease the extent of intramolecular hydrogen bonding; this in turn will facilitate the removal of the hydrogen ion from the ligand and hence decreasing its pK_a value.

When the pK_a values of 2-SPHDEM ligand is plotted as a function of $1/\epsilon$ of the mixed aqueous solvents, a linear relationship was obtained Fig.1. From this linear relation the pK_a of the ligand in water can be determine by extrapolating to $1/\epsilon = 0.013$ ($1/\epsilon$ dielectric constant of water at 25°). The value of pK_a of the ligand obtained from the curve was in good agreement with that obtained experimentally.

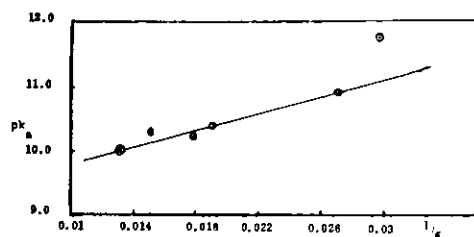


Fig.1: Variation of pK_a for 2-SPHDEM with $1/\epsilon$ at 25°C and 0.1M ionic strength.

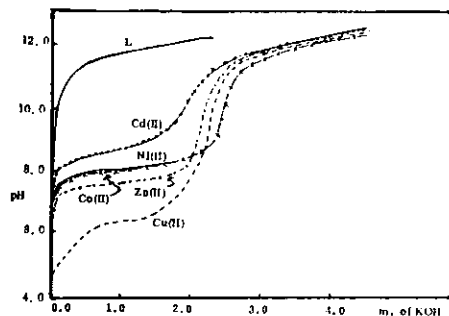


Fig. 2: pH-metric titration of 2×10^{-3} M 2-SPHDEM and 1×10^{-3} M bivalent metal ions with 0.1M. KOH at 25°C and 0.1M.ionic strength.

(2) i) Stability of bivalent metals-2-SPHDEM complexes

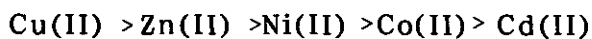
The pH-metric titration curves of the bivalent metal chelates of 2-SPHDEM ligand in 50% (v/v) dioxane-water is given in Fig.2, as an example. A large depression in pH of about five units in case of cupric ion indicates the formation of highly stable chelate compounds than the other metal ions which show less depression in pH (2.0-3.0 units).

The sharp inflection at $m = 2$ (where $m =$ number of moles of KOH added per mole of ligand) confirming the formation of 1:2 complex. The titration of some selected metal ions and ligand in 1:3 ratio showed that the inflection was obtained at $m = 2$, confirming that 1:2 complex is the higher complex formed. Similar behaviour in titration curves was observed using other mixed aqueous solvents.

Table-2: Stability constants of bivalent complexes of 2-SPHDEM in various mixed aqueous solvents at 25°C and 0.1 M ionic strength.

Solvent composition %(v/v)	$\frac{1}{c}$	cons tants	Metal Ions				
			Cu(II)	Ni(II)	Co(II)	Zn(II)	Cd(II)
0.0%(E-W)	0.0130	$\log K_1$	6.50	4.58	4.58	5.24	4.14
		$\log K_2$	6.06	4.14	4.06	4.61	3.66
		$\log \beta_2$	12.56	8.72	8.64	9.85	7.80
25% (E-W)	0.0151	$\log K_1$	6.60	4.74	4.62	5.45	4.40
		$\log K_2$	6.12	4.30	4.17	4.89	3.91
		$\log \beta_2$	12.72	9.04	8.79	10.34	8.31
50%(E-W)	0.0194	$\log K_1$	7.02	5.75	5.67	6.07	5.48
		$\log K_2$	6.53	5.35	5.14	5.63	5.03
		$\log \beta_2$	13.55	11.10	10.81	11.70	10.51
75%(E-W)	0.0271	$\log K_1$	7.60	6.45	6.38	6.55	5.86
		$\log K_2$	7.35	5.79	5.77	5.91	5.38
		$\log \beta_2$	14.95	12.24	12.15	12.46	11.24
50%(M-W)	0.0178	$\log K_1$	6.88	5.43	5.32	5.99	4.95
		$\log K_2$	6.39	4.80	4.73	5.30	4.42
		$\log \beta_2$	13.27	10.23	10.05	11.29	9.37
50%(D-W)	0.0293	$\log K_1$	8.35	6.54	6.72	6.90	5.96
		$\log K_2$	7.60	5.99	6.36	6.33	5.48
		$\log \beta_2$	15.95	12.53	13.08	13.23	11.44

Applying Irving and Rossotti method [11], the successive stability constants $\log K_1$ and $\log K_2$ were calculated which corresponding to 1:1 and 1:2 complexes respectively (Table-2). The order of stability of 2-SPHDEM-metal complexes in all mixed solvent studied was found to be,



which in accordance with that of Irving and Williams [12] with the exceptional that $\text{Zn(II)} > \text{Ni(II)}$ and Co(II) . The order $\text{Zn(II)} > \text{Ni(II)}$ with some organic ligands containing sulphur has been reported by many workers [13-15]. The observed stability order indicates also that Zn(II) forms stronger complexes than Ni(II) , Co(II) and Cd(II) .

This behaviour may be explained on the basis that the metal-ligand bond in the former case is more of π -type of bond with the back donation of electrons from these metal ions to the ligand [16].

ii) Solvent Effect on Chelation

Table-2 shows that the 2-SPHDEM complexes of bivalent metal ions studied are more stable in mixed aqueous organic solvents than in water. The successive stability constants ($\log K_1$ and $\log K_2$) as well as $\log \beta_2$ (overall stability constant) in different mixed solvents follow the order : 50% dioxane-water > 50% ethanol-water > 50% methanol-water, on the other hand, for a particular mixed

solvent e.g. ethanol, the order of stability is:

75% ethanol-water > 50% ethanol-water > 25% ethanol-water.

This is in agreement with the expectation that the stability of complexes decreases with increasing the dielectric constants of the solvent. The decrease of the stability constants of the formed complexes by increasing the percentage of water (i.e. increasing the extent of solvation of the metal ions by water molecules [6]). In addition the presence of water molecules will facilitate the formation of intermolecular hydrogen bonding between water and ligand molecules and hence will lower the degree of complexation. The lowering of dielectric constant would increase the electrostatic force of attraction between the metal ion and the negativity charged to form more stable 1:1 and 1:2 complexes. The stability constants ($\log K_1$) for Cu(II), Ni(II), Co(II), Zn(II) and Cd(II)-2-SPHDEM complexes increase linearly with $1/\epsilon$ of the solvent (Fig. 3).

3) Interaction of Lanthanide (III) ions with 2-SPHDEM

The titration of 1 : 3 (metal : ligand) in 50% (v/v) ethanol water solvent at 25°C and 0.1M ionic strength resulted in a sharp inflection at $m = 2$ ($m =$ number of moles of KOH added per mole of ligand) corresponding to the formation of 1:2 complexes. This confirms that the ligand behaves as monoprotic ligand and that 1:2 (metal : ligand) complexes are the most predominant. From the titration curves \bar{n} (average number of ligand molecules attached per metal ion) and pL (free ligand exponent) values were calculated applying Irving and Rossotti method [11]. The \bar{n} values were plotted against the corresponding pL

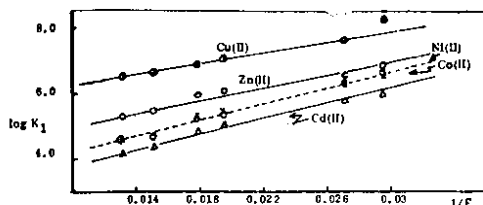


Fig.3: Variation of $\log K_1$ for 2-SPHDEM-bivalent metal complexes with $1/\epsilon$.

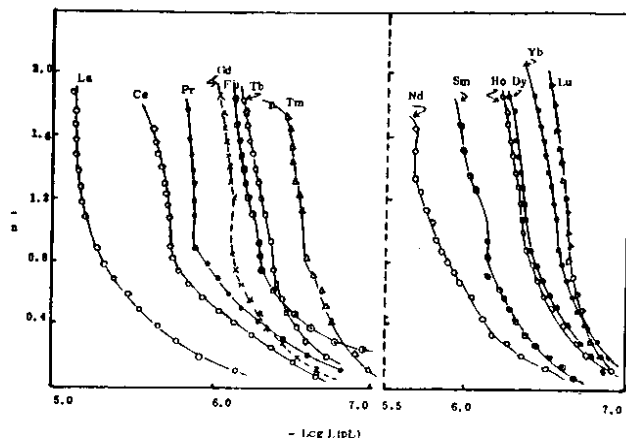
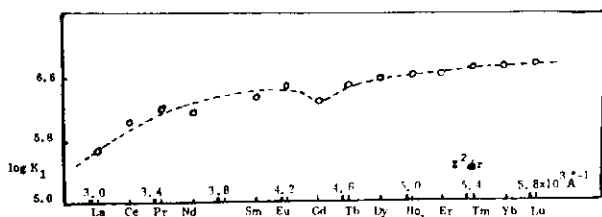


Fig.4: Metal-Ligand system of 2-SPHDEM formation curves.

values to get the formation curves of metal complex equilibria, (Fig. 4). From these formation curves, the values of stability constants $\log K_1$ and $\log K_2$ were evaluated which correspond to 1 : 1 complexes at $\bar{n} = 0.5$ and 1 : 2 complex at $\bar{n} = 1.5$ respectively. These were further correlated by plotting $\log \frac{\bar{n}}{1-\bar{n}}$ vs pL and $\log \frac{2-\bar{n}}{\bar{n}-1}$ vs pL graphs respectively. The values of $\log K_1$ and $\log K_2$ evaluated from the linear plots agree quite well with those obtained by half integral method. The most representative values of $\log K_1$, $\log K_2$ and $\log \beta_2$ for 1 : 1 and 1 : 2 complexes formed between lanthanide ions and the organic ligand (2-SPHDEM) are given in Table-3.

Table-3: Stability constants of Lanthanides (II)-2-SPHDEM complexes in 50% (v/v) Ethanol-water solvent and 0.1M ionic strength at 25°C.

Metal ion	log K ₁	log K ₂	log β ₂	log K ₁ /K ₂	ΔG ₁ [*]
La ³⁺	5.56	5.13	10.69	1.08	31.28
Ce ³⁺	6.04	5.64	11.68	1.07	33.99
Pr ³⁺	6.18	5.85	12.03	1.06	34.78
Nd ³⁺	6.08	5.70	11.78	1.07	34.22
Sm ³⁺	6.28	5.99	12.27	1.05	35.34
Eu ³⁺	6.50	6.16	12.66	1.06	36.58
Gd ³⁺	6.28	6.08	12.36	1.03	35.34
Tb ³⁺	6.46	6.23	12.69	1.04	36.36
Dy ³⁺	6.58	6.30	12.88	1.04	37.03
Ho ³⁺	6.57	6.28	12.85	1.05	36.98
Er ³⁺	6.56	6.24	12.80	1.05	36.92
Tm ³⁺	6.70	6.50	13.20	1.03	37.71
Yb ³⁺	6.70	6.48	13.18	1.03	37.71
Lu ³⁺	6.72	6.52	13.24	1.03	37.82

* ΔG₁ in K.J./mole.Fig.5: Plots of log K₁ vs. ionization potential of trivalent lanthanide (Z^2/r).

As the tendency of the metal ion to take the organic ligand is proportional to the number of vacant sites, the ratio between consecutive constants $\log K_1/K_2$, to a certain extent is the stability determined [17] as shown in Table-3 where for all chelates studied, $\log K_1 - \log K_2$ is positive value.

Rare earths normally form ionic compounds, but the possibility of covalent interaction cannot completely excluded as reported previously [18]. If the bonds are ionic, the Born relation $E = Z^2/2r (1 - \frac{1}{\epsilon})$ should hold for the

energy change on complexation of a gaseous ion of charge "Z" and radius "r" in a medium of dielectric constant "ε". Since the stability constant is related directly to this energy, the log K's (K_1 , K_2 and β_2) values should increase linearly with Z^2/r . In the present investigation the plot of Z^2/r vs $\log K_1$ or $\log \beta_2$ values (Fig.5) shows a linear increase of $\log K_1$ and $\log \beta_2$ with Z^2/r only in the first part of the curve from (La³⁺ - Eu³⁺). This indicates that the stability of the complex formed was directly proportional to the total ionization potential of the central metal atom. The second part of the curve (Tb³⁺ - Lu³⁺) shows a buffer zone (almost constant stability). This behaviour has been reported in the literature [19-21].

The deviation from linearity beyond Gd(III) observed in the present study is also in agreement with observations cited earlier [22,23].

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