

## Formation of Zinc and Cadmium Chelates of Nitro- naphthols in Aqueous Solution

### Part III. Spectrophotometry of the Chelates of 2-Nitroso-1-naphthol and Its Sulphonic Acids

HEIKKI SAARINEN and OSMO MÄKITIE

*Department of Inorganic Chemistry, University of Helsinki, Helsinki, Finland*

The formation of zinc and cadmium chelates of 2-nitroso-1-naphthol, 2-nitroso-1-naphthol-4-sulphonic acid, 2-nitroso-1-naphthol-5-sulphonic acid, 2-nitroso-1-naphthol-8-sulphonic acid, and 2-nitroso-1-naphthol-4,8-disulphonic acid were studied spectrophotometrically. The logarithms of the stability constants ( $\beta_1 = [ML]/[M][L]$ ) of the first zinc chelates in aqueous solution at 25°C and at ionic strength 0.1 (KCl) were found to be (ligands in the order mentioned): 3.91, 3.56, 3.82, 4.05, and 3.80. The values for the cadmium chelates were: 3.33, 3.08, 3.22, 3.40, and 3.25, respectively.

The values of the naphtholic dissociation constants of all the ligands, except 2-nitroso-1-naphthol-4-sulphonic acid, for which the constant had been determined previously, were also determined spectrophotometrically.

The absorption spectra of the metal chelates are presented and the results are discussed.

In the earlier parts of this series of investigations, the formation of the zinc chelates of 1-nitroso-2-naphthol-6-sulphonic acid (Nitroso-Schäffer's acid) and 2-nitroso-1-naphthol-5-sulphonic acid (Nitroso-C acid),<sup>1</sup> as well as the formation of zinc and cadmium chelates of 2-nitroso-1-naphthol-8-sulphonic acid and 2-nitroso-1-naphthol-4,8-disulphonic acids were studied potentiometrically.<sup>2</sup> The work has now been continued by the spectrophotometric method. Results of studies on complex formation by ligands of the 2-nitroso-1-naphthol type are reported in this paper.

The studied sulpho derivatives of 2-nitroso-1-naphthol are the following (trivial names derived from the trivial names of the naphtholsulphonic acids are given in parentheses):

2-Nitroso-1-naphthol-4-sulphonic acid [Nitroso-NW (Neville-Winther's acid)],

2-Nitroso-1-naphthol-5-sulphonic acid (Nitroso-C acid),

2-Nitroso-1-naphthol-8-sulphonic acid [Nitroso-S ( $\alpha$ -naphtholsulphonic acid S) acid], and

2-Nitroso-1-naphthol-4,8-disulphonic acid (Nitroso-Schöllkopf's acid).

All the ligands form relatively strong chelates with zinc and cadmium ions.

#### EXPERIMENTAL

*Reagents.* 2-Nitroso-1-naphthol ("zur Analyse", from E. Merck AG) was purified by recrystallization first from a water-methanol mixture and then twice from water. The preparation was dried under vacuum.

2-Nitroso-1-naphthol-4-sulphonic acid, sodium salt (a reagent from The British Drug Houses Ltd.) was recrystallized from water.

Sodium 2-nitroso-1-naphthol-5-sulphonate was prepared by nitrosation of the sodium salt of C-acid (1-naphthol-5-sulphonic acid, sodium salt, a reagent from The British Drug Houses Ltd.) as described previously.<sup>1</sup>

Sodium 2-nitroso-1-naphthol-8-sulphonate and disodium 2-nitroso-1-naphthol-4,8-sulphonate were prepared from 1-aminonaphthalene-8-sulphonic acid (a reagent from Fluka AG) and 4-aminonaphthalene-1,5-disulphonic acid (a reagent from Aldrich Chemical Co., Inc.), respectively, by way of the intermediate diazo compounds as described recently.<sup>2</sup>

The zinc and cadmium salts were the perchlorates, the metal of which was checked by EDTA titrations. Potassium chloride was used as neutral salt to increase the ionic strengths of the solutions.

*Apparatuses and methods.* The measurements were carried out with a Beckman Model DU monochromator/Gilford photometer apparatus using calibrated 10-mm quartz cells. The absorption spectra were recorded with a Beckman Model DK 2A recording spectrophotometer.

A Radiometer Model PHM 4d potentiometer connected to a Beckman glass electrode and an open liquid junction reference calomel electrode filled with saturated potassium chloride solution was used to measure the pH values. The hydrogen ion concentrations were calculated by means of apparent activity coefficient values given by Näsänen *et al.*<sup>3</sup>

The experiments were carried out at 25°C.

Customary spectrophotometric methods were used to determine the dissociation constants of the acids and the formation constants of the first metal chelates (see, *e.g.*, Ref. 4).

#### RESULTS AND DISCUSSION

2-Nitroso-1-naphthol-4-sulphonic acid is the strongest of the five acids (naphtholic dissociation), and 2-nitroso-1-naphthol-8-sulphonic acid is the weakest. 2-Nitroso-1-naphthol itself is a much weaker acid than the former, but clearly stronger than the latter acid.

The values of the acid dissociation constants obtained spectrophotometrically in the present study are in accordance with the values reported previously. The thermodynamic values at 25°C,  $pK_2^0 = 7.32$  for 2-nitroso-1-naphthol-5-sulphonic acid,<sup>1</sup>  $pK_2^0 = 8.19$  for 2-nitroso-1-naphthol-8-sulphonic acid, and  $pK_3^0 = 7.32$  for 2-nitroso-1-naphthol-4,8-disulphonic acid were previously obtained from potentiometric data.<sup>2</sup> The spectrophotometric values obtained now,  $pK_2 = 6.894$  (Table 2),  $pK_2 = 7.730$ , and  $pK_3 = 6.671$  for 2-nitroso-1-naphthol-5-sulphonic acid,<sup>1</sup> 2-nitroso-1-naphthol-8-sulphonic acid and 2-nitroso-1-naphthol-4,8-disulphonic acid,<sup>2</sup> respectively, can be compared with the potentiometric values 6.91, 7.74, and 6.66 at the same ionic strength 0.1.

Table 1.  $pK_a$  values for 2-nitroso-1-naphthol in solutions of varying ionic strength (KCl, 25°C),  $c_{\text{phosphate buffer}} = 3.3 \times 10^{-3}$  M.

$\sqrt{I}$	0.123	0.315	0.505	0.796	1.122	1.417
$pK_a(\text{calc.})$	7.355	7.255	7.206	7.193	7.243	7.336
$pK_a(\text{obs.})$	7.363	7.243	7.205	7.195	7.248	7.332

For 2-nitroso-1-naphthol itself, however, we derived from the spectrophotometric data at 25°C, shown in Table 1, the Debye-Hückel equation

$$pK_a^0 = 7.458 = pK_a + 1.018 \sqrt{I} / (1 + 1.46 \sqrt{I}) - 0.17I \quad (1)$$

The value 7.46 differs slightly from the thermodynamic value 7.38 extrapolated by Dyrssen and Johansson.<sup>5,6</sup> However, the experimental value for 2-nitroso-1-naphthol reported by them,  $7.24 \pm 0.02$  ( $I = 0.1$ ,  $\text{NaClO}_4$ , 25°C)<sup>5</sup> is equal to the value 7.25 ( $I = 0.1$  KCl, 25°C; Table 1) we obtained. The only other value for 2-nitroso-1-naphthol (in aqueous solution) given in the literature seems to be 7.59 (25°C), reported by Trübsbach.<sup>7</sup>

Table 2. Evaluation of the dissociation constant (as  $pK_2$ ) of 2-nitroso-1-naphthol-5-sulphonic acid in aqueous solution from absorbances measured at wavelengths in the range 410–490 nm (25°C).  $I = 0.10$ ,  $c_{\text{phosphate buffer}} = 6.7 \times 10^{-3}$  M.

$-\log[H^+]$	410	420	430	440	$\epsilon \times 10^{-3}$					$pK_2$
					450	460	470	480	490 nm	
(HL <sup>-</sup> )	3.35	2.81	2.12	1.52	0.99	0.61	0.40	0.26	0.18	
(L <sup>2-</sup> )	7.49	8.40	8.88	8.73	7.97	6.89	5.47	4.01	2.80	
6.56	4.69	4.61	4.29	3.81	3.20	2.61	2.01	1.46	1.02	6.89
6.75	5.10	5.17	4.95	4.54	3.92	3.23	2.52	1.83	1.28	6.89
6.84	5.29	5.43	5.31	4.88	4.25	3.54	2.77	2.03	1.42	6.90
6.91	5.45	5.65	5.56	5.17	4.51	3.78	2.95	2.15	1.50	6.89
7.06	5.82	6.14	6.18	5.82	5.17	4.34	3.39	2.48	1.74	6.89
										Mean =
	6.89	6.89	6.89	6.90	6.90	6.90	6.90	6.90	6.89	6.894

The  $pK_2^0$  value for 2-nitroso-1-naphthol-4-sulphonic acid obtained by potentiometric and spectrophotometric methods is 6.50 (25°C).<sup>8</sup>

The  $pK_a$  values for these ligands at ionic strength 0.1 are listed in Table 4. Absorption spectra showing the course of the protolysis of 2-nitroso-1-naphthol-4,8-disulphonic acid are reproduced in Fig. 1.

The formation constants

$$K_I = [\text{ML}^{(n-2)-}] [\text{H}^+] / [\text{M}^{2+}] [\text{L}^{n-}] \quad (2)$$

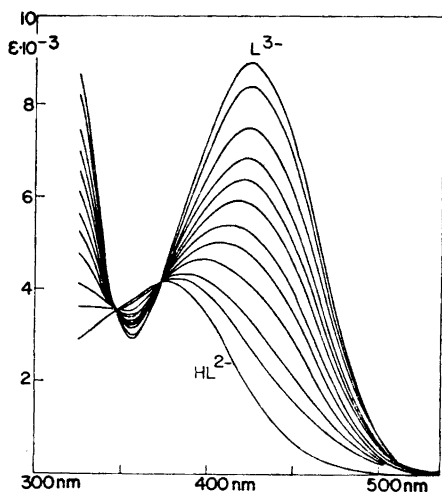


Fig. 1. The variation of the absorption spectrum of an aqueous solution of 2-nitroso-1-naphthol-4,8-disulphonic acid with pH.

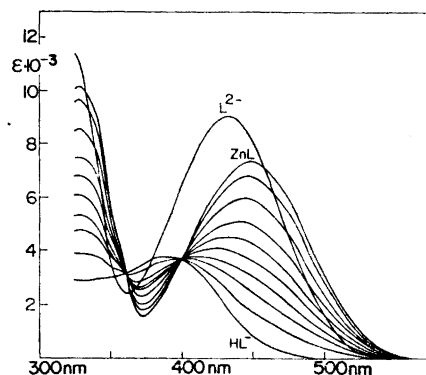


Fig. 2. Spectra relating to the formation of the first zinc chelate of 2-nitroso-1-naphthol-5-sulphonic acid.

of the zinc and cadmium chelates in aqueous solutions of ionic strength 0.1 were determined spectrophotometrically using relative high metal:ligand ratio. The data in Table 3 were obtained for the first zinc chelate of 2-nitroso-1-naphthol-8-sulphonic acid. The absorption spectra in Figs. 1 and 2 show the shifts of the absorption peaks towards longer wavelengths as the metal chelation progresses.

The  $pK_I$  values and the values of the stability constants ( $\beta = [ML^{(n-2)}-]/[M^{2+}][L^{n-}]$ ) are listed in Table 4. Callahan *et al.* and Van Uitert *et al.* studied the formation of metal chelates of 2-nitroso-1-naphthol in water-dioxan mixtures.<sup>9,10</sup> Tolmachev *et al.* studied the formation of metal chelates, but not the zinc or cadmium chelates, of 2-nitroso-1-naphthol-4-sulphonic acid.<sup>11</sup>

Table 3. Evaluation of the equilibrium constant (as  $pK_I$ ) for the formation of the first zinc chelate of 2-nitroso-1-naphthol-8-sulphonic acid in aqueous solution from absorbances measured at wavelengths in the range 420–500 nm (25°C).  $c = 9.31 \times 10^{-5}$ ,  $c_{Zn}:c = 16.09$ ,  $I = 0.10$ .

$-\log[H^+]$	$pK_I$ (at nm)									$pK_I$
	420	430	440	450	460	470	480	490	500	
6.35	3.68	3.68	3.69	3.69	3.69	3.70	3.70	3.68	3.68	3.69
6.43	3.67	3.67	3.67	3.67	3.67	3.67	3.66	3.65	3.65	3.67
6.55	3.69	3.68	3.68	3.68	3.68	3.69	3.69	3.69	3.68	3.68
6.77	3.68	3.67	3.67	3.68	3.67	3.69	3.69	3.69	3.69	3.68
	3.68	3.68	3.68	3.68	3.68	3.69	3.69	3.68	3.68	Mean = 3.682

Table 4. The dissociation constants of the ligands and the formation constants and stability constants of their zinc and cadmium chelates at ionic strength 0.1 (KCl, 25°C).

Ligand	$pK_a$	Zinc chelate $pK_I$	$\log \beta_1$	Cadmium chelate $pK_I$	$\log \beta_1$
2-Nitroso-1-naphthol	7.25	3.34	3.91	3.92	3.33
2-Nitroso-1-naphthol-4-sulphonic acid	6.10	2.54	3.56	3.02	3.08
2-Nitroso-1-naphthol-5-sulphonic acid	6.89	3.07	3.82	3.67	3.22
2-Nitroso-1-naphthol-8-sulphonic acid	7.73	3.68	4.05	4.33	3.40
2-Nitroso-1-naphthol-4,8-disulphonic acid	6.67	2.87	3.80	3.42	3.25

Table 5. Spectral data at 25°C.

	2-Nitroso-1-naphthol	2-Nitroso-1-naphthol-4-sulphonic acid	2-Nitroso-1-naphthol-5-sulphonic acid	2-Nitroso-1-naphthol-8-sulphonic acid	2-Nitroso-1-naphthol-4,8-disulphonic acid
(L) $\lambda_{\max}$ (at nm)	430	428	431	426	426
(ZnL) $\lambda_{\max}$ (at nm)	451	439	449	453	444
(CdL) $\lambda_{\max}$ (at nm)	439	433	440	445	440
(L) $\epsilon \times 10^{-3}$ (at $\lambda_{\max}$ )	8.74	10.10	8.91	7.76	8.94
(ZnL) $\epsilon \times 10^{-3}$ (at $\lambda_{\max}$ )	7.01	8.64	7.38	6.66	7.78
(CdL) $\epsilon \times 10^{-3}$ (at $\lambda_{\max}$ )	7.36	8.99	7.64	6.77	8.03
Isosbestic points:					
HL/L (nm)	357;379	348;379	353;379	353;373	347;373
HL/ZnL (nm)	368;405	360;392	360;399	367;408	357;396
HL/CdL (nm)	368;396	361;385	360;393	368;401	354;390

The spectrophotometric results presented in this paper can be compared with those reported by us previously. In the case of 2-nitroso-1-naphthol-8-sulphonic acid and 2-nitroso-1-naphthol-4,8-disulphonic acid, the  $pK_I$  values of zinc and cadmium chelates are in good agreement with those obtained potentiometrically.<sup>2</sup> The lower values obtained spectrophotometrically for chelates of 2-nitroso-1-naphthol-4-sulphonic acid and 2-nitroso-1-naphthol-5-sulphonic acid<sup>1,8</sup> indicate that the interpretation of the potentiometric data does not apparently completely cover all possible chelatespecies existing in the solutions when the metal:ligand ratio is low, as it is in potentiometric titrations. In the spectrophotometric measurements it is necessary to use metal ions in excess.

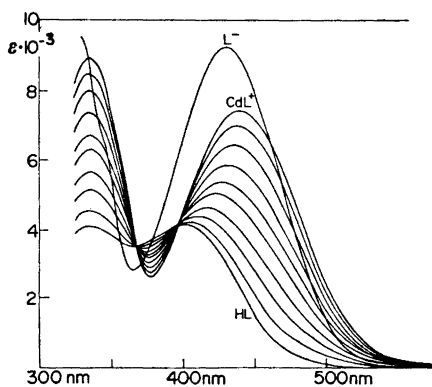


Fig. 3. Spectra relating to the formation of the first cadmium chelate of 2-nitroso-1-naphthol in aqueous solution.

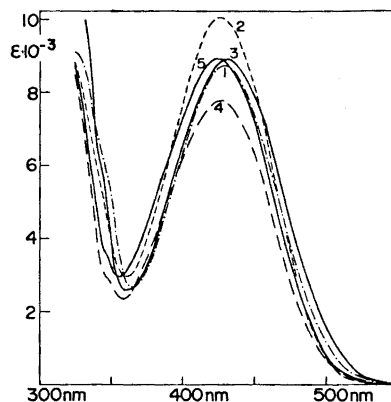


Fig. 4. The absorption spectra of the ligands in alkaline solutions. 1, 2-Nitroso-1-naphthol; 2, 2-nitroso-1-naphthol-4-sulphonate; 3, 2-nitroso-1-naphthol-5-sulphonate; 4, 2-nitroso-1-naphthol-8-sulphonate; 5, 2-nitroso-1-naphthol-4,8-disulphonate.

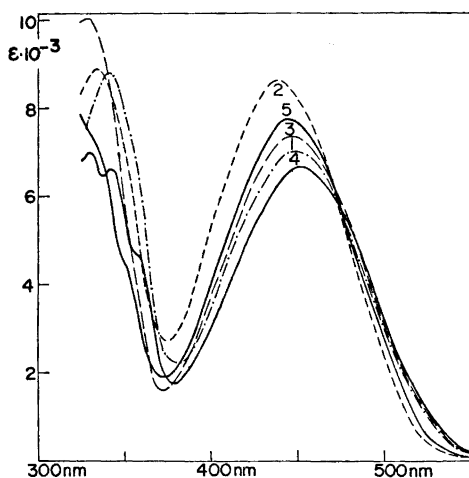


Fig. 5. The absorption spectra of the first zinc chelates of the acids in aqueous solutions. 1,  $ZnL^+$  of 2-nitroso-1-naphthol; 2,  $ZnL$  of 2-nitroso-1-naphthol-4-sulphonic acid; 3,  $ZnL$  of 2-nitroso-1-naphthol-5-sulphonic acid; 4,  $ZnL$  of 2-nitroso-1-naphthol-8-sulphonic acid; 5,  $ZnL^-$  of 2-nitroso-1-naphthol-4,8-disulphonic acid.

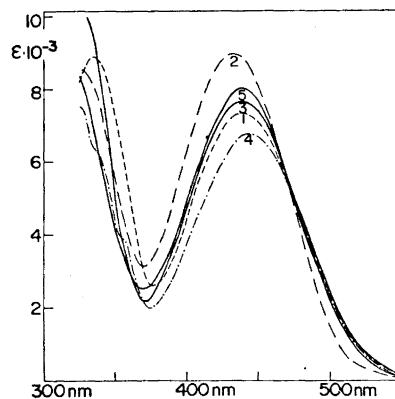


Fig. 6. The absorption spectra of the first cadmium chelates of the acids in aqueous solutions. The numbers of the curves are the same as those of the corresponding curves in Fig. 5.

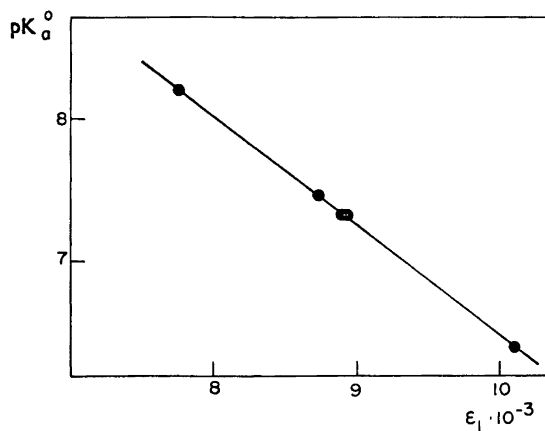


Fig. 7.  $pK_a$  values of the ligand acids as functions of molar absorptivity.

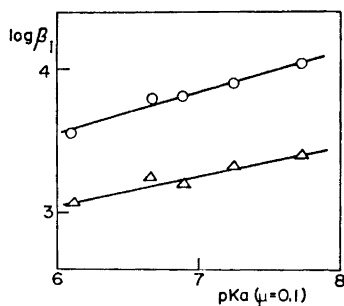


Fig. 8. The relations between the stability values of the first zinc and cadmium chelates and the strengths of the ligand acids at ionic strength 0.1.  $\circ$  = Zinc chelates;  $\triangle$  = cadmium chelates.

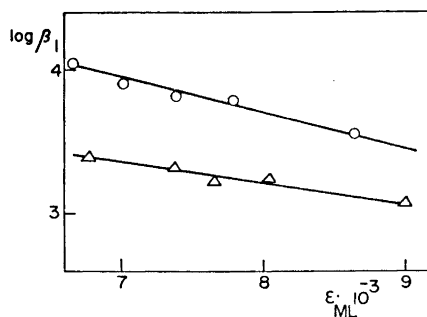


Fig. 9. The stability constant values of the chelates as functions of molar absorptivity in the chelate spectra.  $I=0.1$ ;  $\circ$  = zinc chelates;  $\triangle$  = cadmium chelates.

Spectral data for the ligands and metal chelates are listed in Table 5. Illustrative absorption spectra relating to the formation of zinc and cadmium chelates are shown in Figs. 2 and 3. The spectra of all dissociated forms of the ligand acids are collected in Fig. 4. Figs. 5 and 6 show the absorption spectra of the different metal chelates.

The absorptivities at the last peaks at the wavelengths 400–450 nm in the spectra are correlated with the strengths of the ligand acids and with the stability constants of the first chelates. Fig. 7 shows the linearity of the plot of  $pK_a$  against molar absorptivity. The stability constants of the chelates are plotted as a function of the strength of the ligand in Fig. 8 and the stability constants of the chelates as a function of the molar absorptivity in Fig. 9.

The expected sequences of the acid strengths of the ligands and the stability constants of the zinc and cadmium chelates are nicely reflected in the absorption spectra when the same chelating grouping exists in all the ligands.

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