

## Formation of Praseodymium and Neodymium Chelates of Nitroso-C Acid and Nitroso-Schäffer's Acid in Aqueous Solution

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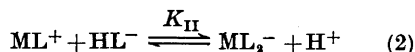
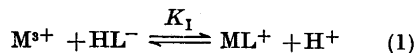
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Nitroso-C acid (2-nitroso-1-naphthol-5-sulphonic acid) and Nitroso-Schäffer's acid (1-nitroso-2-naphthol-6-sulphonic acid) are water-soluble mono-sulpho derivatives of isomeric *ortho*-nitrosophenols that readily form metal chelates.<sup>1</sup> Potentiometric studies of chelate formation by these ligands with trivalent praseodymium and neodymium ions were carried out to determine whether the stabilities of the metal chelates differ greatly.

Table 1. Formation constants evaluated from titration data. [Sodium salt of Nitroso-C acid] =  $4.85 \times 10^{-3}$ M,  $[\text{Nd}(\text{ClO}_4)_3] = 1.20 \times 10^{-3}$ M,  $I = 0.0087$ ,  $25^\circ\text{C}$ .

$c_B:c_{\text{Nd}}$	$-\log[\text{H}^+]$	
0.292	4.608	$pK_{\text{I}} = 2.66$
0.383	4.738	2.63
0.484	4.871	2.61
0.583	5.010	2.62
0.687	5.150	2.62
0.800	5.299	2.64
1.255	5.872	$pK_{\text{II}} = 3.85$
1.358	5.997	3.89
1.467	6.109	3.90
1.587	6.213	3.88
1.692	6.310	3.89
1.817	6.401	3.86
$(pK_{\text{III}} \sim 4.95)$		

The titration data presented in Table 1 show that the metal chelate formation can be interpreted by assuming the occurrence of the successive chelation reactions;



Plots of the first formation constants (eqn. 1) are shown in Fig. 1. The thermodynamic values were determined by means of the equation

$$pK_{\text{I}}^\circ = pK_{\text{I}} - \frac{4.072 \sqrt{I}}{1 + 1.13 \sqrt{I}} + 0.38I \quad (3)$$

the parameter values ( $\alpha = 1.13$  and  $B = 0.38$ ) of which were computed from data obtained for the chelate  $\text{PrL}^+$  of Nitroso-C acid. As expected the values of the second formation constant (eqn. 2) did not vary with ionic strength.

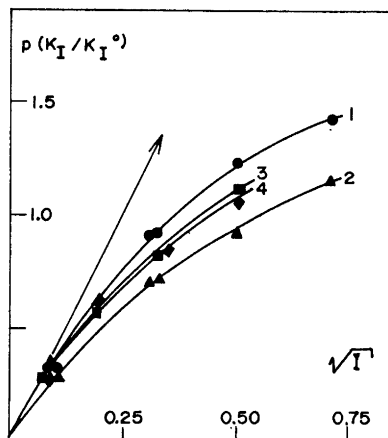


Fig. 1. Plots of  $p(K_{\text{I}}/K_{\text{I}}^\circ)$  as a function of the square root of ionic strength for  $\text{PrL}^+$  (1) and  $\text{NdL}^+$  (2) of Nitroso-C acid and  $\text{PrL}^+$  (3) and  $\text{NdL}^+$  (4) of Nitroso-Schäffer's acid.

Table 2 shows the corresponding stability constants ( $\beta_1 = [\text{ML}^+]/[\text{M}^{3+}][\text{L}^{2-}]$  and  $\beta_2 = [\text{ML}_2^-]/[\text{M}^{3+}][\text{L}^{2-}]^2$ ) at ionic strength 0.1. Values of these constants are plotted as functions of the square root of ionic strength in Fig. 2.

The praseodymium chelates are more stable than the neodymium chelates. Nitroso-Schäffer's acid forms much stronger chelates than Nitroso-C acid. Nitroso-Schäffer's acid is also the weaker acid.

Table 2. Stability constants of the chelates at ionic strength 0.1 (KCl) and 25°C.

	$pK_a(HL^-)$	$pK_I$	$\log\beta_1$	$\log\beta_2$
Nitroso-C acid:	6.91			
PrL <sup>+</sup>		3.41	3.50	6.3
NdL <sup>+</sup>		3.08	3.83	6.9
Nitroso-Schäffer's acid:	7.22			
PrL <sup>+</sup>		2.97	4.25	7.7
NdL <sup>+</sup>		2.70	4.52	8.2

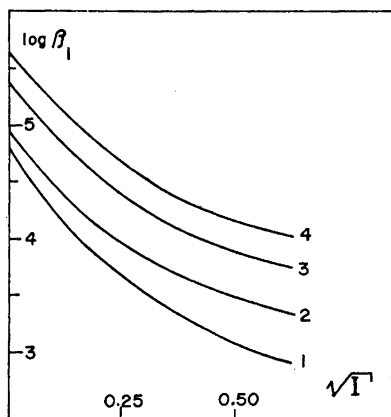


Fig. 2. Stability constants of the first lanthanide chelates as functions of the square root of ionic strength. The numbering of the plots is the same as in Fig. 1.

The values  $\log \beta_1 = 5.01$  ( $I = 0.1$ ) for the chelate NdL of 1-nitroso-2-naphthol-3,6-disulphonic acid (Nitroso-R acid) and  $\log \beta_1 = 3.47$  for the chelate NdL<sup>+</sup> of 2-nitroso-1-naphthol-4-sulphonic acid at 25°C have been reported in previous papers.<sup>2</sup> Callahan *et al.* have reported

stability constants for praseodymium and neodymium chelates of 1-nitroso-2-naphthol and 2-nitroso-1-naphthol in dioxan-water mixtures.<sup>3</sup>

*Experimental.* Nitroso-C acid was prepared by nitrosation of the sodium salt of C-acid (1-naphthol-5-sulphonic acid, a purified reagent from B.D.H.), and Nitroso-Schäffer's acid by nitrosation of sodium 2-naphthol-6-sulphonate (a purified reagent from B.D.H.).<sup>1</sup>

Praseodymium perchlorate and neodymium perchlorate (prepared from Pr<sub>6</sub>O<sub>11</sub> and Nd<sub>2</sub>O<sub>3</sub>, reagents from B.D.H., which were labeled 99.9% pure) were used as the metal salts.

A 0.1 M sodium hydroxide solution was used as titrant. Potassium chloride was added to increase the ionic strengths of the solutions.

The apparatuses and methods have been described earlier.<sup>1</sup> The following equations were used to calculate the values of the second dissociation constants of the ligand acids:<sup>1</sup> For Nitroso-C acid,

$$pK_2 =$$

$$7.32 - 2.036 \sqrt{I} / (1 + 1.34 \sqrt{I}) + 0.42I \quad (4)$$

and for Nitroso-Schäffer's acid

$$pK_2 =$$

$$7.60 - 2.036 \sqrt{I} / (1 + 1.87 \sqrt{I}) + 0.24I \quad (5)$$

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2. Mäkitie, O. *Suomen Kemistilehti* **B 40** (1967) 267; **B 41** (1968) 31.
3. Callahan, C. M., Fernelius, W. C. and Block, B. P. *Anal. Chim. Acta* **16** (1957) 101; *Stability Constants of Metal-Ion Complexes*, The Chemical Society, London, Special Publ. 17, 1964.

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