ABSTRACT

This thesis examines the formation and dissociation reactions of mono-nickel sulphonated complexes of 1-nitroso-2-naphthol ligands.

The kinetics of the formation and dissociation reactions of Ni(II) complexes and the general properties of nitrosonaphthols and their reactions with metal ions are reviewed.

The ligands were prepared from the appropriate naphthol-sulphonic acids by nitrosation. An improved synthesis of 1-nitroso-2-naphthol-3-sulphonic acid is reported. The spectral properties of the ligands were investigated and reported.

The acid dissociation constants of all the nitrosonaphthols, in the temperature range 20.0°C - 30.0°C and at 0.1M ionic strength, were measured spectrophotometrically. The formation constants of the 1:1 nickel complexes were also measured at 25.0°C, spectrophotometrically.

The pK_a and K_{NiL} values at 25.0°C and I = 0.1M are shown below:

LIGANDS	pK_a	K_{NiL}
1-nitroso-2-naphthol-3-sulphonate	7.57	0.35
1-nitroso-2-naphthol-4-sulphonate	7.20	0.23
1-nitroso-2-naphthol-5-sulphonate	7.16	0.13
1-nitroso-2-naphthol-7-sulphonate	7.29	0.41
2-nitroso-1-naphthol-4,6-disulphonate	5.90	0.43

The pK_a values do not show a large variation with temperature. The effect of ionic strength on K_{NiL} was investigated for Ni(1-nitroso-2-naphthol-3-sulphonate) and Ni(1-nitroso-2-naphthol-4-sulphonate). The values of K_{NiL} of Ni(1-nitroso-2-naphthol-3-sulphonate) are 0.39 and 0.38 at 0.02M and 0.05M ionic strength respectively, whereas the values for Ni(1-nitroso-2-naphthol-4-sulphonate) are 0.29 and 0.28 at 0.02M and 0.05M ionic strength respectively.

The dissociation kinetics of the 1:1 Ni-nitrosonaphthol complexes were investigated in acidic aqueous solution in the temperature range 20.0°C - 30.0°C. The effect of ionic strength on the dissociation rates were also examined. The unusual behaviour of the dissociation of Ni(1-nitroso-2-naphthol-3-sulphonate) with respect to ionic strength is reported and discussed.

The rate expression for the dissociation reaction was found to follow the equation given below:

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{1}{C[H^+]}$$

where k_1 is the rate constant for chelate ring opening and C is a collection of rate and equilibrium constants.

The values of k_1 and C at 25.0°C are given as follows:

COMPLEX	k_1, s^{-1} (10^{-3}C) 20.0°C	25.0°C	30.0°C
Ni(1-nitroso-2-naphthol-3-sulphonate)	489, (1.35)	617, (1.62)	792, (2.26)
Ni(1-nitroso-2-naphthol-4-sulphonate)	547, (1.22)	706, (1.44)	1045, (1.94)
Ni(1-nitroso-2-naphthol-5-sulphonate)	463, (0.85)	579, (1.07)	830, (1.39)
Ni(1-nitroso-2-naphthol-7-sulphonate)	562, (1.23)	617, (1.60)	756, (2.06)
Ni(2-nitroso-1-naphthol-4, 6-disulphonate)	247, (1.02)	488, (1.23)	601, (1.62)

Enthalpies and entropies of activation for the dissociation reactions are reported.

The kinetics of formation of the various 1:1 Ni(II)-nitroso-naphthol complexes were investigated in the temperature range 20.0° - 30.0°C. All the ligands react at very similar rates except the 3-sulphonate ligand, where the formation rate constant has been found to be higher than the other sulphonated derivatives.

The variation of the rate constants with hydrogen ion concentration for the formation reaction was fitted by non-linear least square analysis which allows the determination of k_{12} and k_{43}. Enthalpies and entropies for these formation reactions have also been reported.

The specific rate constants for the formation of 1:1 nickel (II) complexes at 25°C and 0.1M ionic strength are shown below:

COMPLEX	$10^{-3}k_{12}$, $M^{-1}s^{-1}$	$10^{-4}k_{43}$, $M^{-1}s^{-1}$
Ni(1-nitroso-2-naphthol-3-sulphonate)	3.61 (± 0.52)	13.6 (± 0.99)
Ni(1-nitroso-2-naphthol-4-sulphonate)	3.75 (± 0.29)	6.18 (± 0.26)
Ni(1-nitroso-2-naphthol-5-sulphonate)	3.76 (± 0.44)	3.98 (± 0.24)
Ni(1-nitroso-2-naphthol-7-sulphonate)	3.70 (± 0.30)	5.89 (± 0.28)

N.B. The terms in the brackets are standard deviations.

The effect of ionic strength on the rate of formation of Ni(1-nitroso-2-naphthol-3-sulphonate) and Ni(1-nitroso-2-naphthol-4-sulphonate) was studied and was found to show the expected behaviour.

The relatively high value of k_{43} for Ni(1-nitroso-2-naphthol-3-sulphonate) is interpreted as being due to enhanced ion-pair formation due to the position of sulphonate group in the 3-position.