

Potentiometric Studies on the Complexes of Some Divalent Metal Ions and Rare Earth Metal Ions with 3-Methyl-2-thio-2,4(1H, 3H)-quinazolinedione[†]

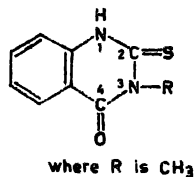
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Manuscript received 19 July 1983, revised 16 December 1983, accepted 3 May 1984

Potentiometric studies have been carried out on 3-methyl-2-thio-2,4(1H,3H)-quinazolinedione as ligand for complexation with divalent metal ions like Zn^{II}, Cd^{II}, Ni^{II}, Mn^{II} and some rare earth metal ions like Nd^{III}, Sm^{III}, Gd^{III}, Dy^{III}. The proton-ligand and metal-ligand stability constants have been determined by Bjerrum's method at 27 ± 1° and at ionic strength 0.1 M in 3 : 1 (v/v) dioxan-water medium. The order of stability constants observed is in agreement with the order reported by previous workers. In case of rare earth metal ions the stability constants are higher as compared to the divalent metal ions studied, thereby indicating more ionic character.

2-Thio-2,4(1H, 3H)-quinazolinedione and its substituted derivatives are heterocyclic compounds having allied structures with those of thioxo-imidazolidinones (2-thiohydantoin). In the present investigation the compound is prepared with the idea to use it as complexing agent. The structure is represented as



In the above structure 1-position is not substituted and thus the tautomeric form N(1) through >C=S is maintained giving rise to thio group, from where proton dissociates making provision for the complexation with the metal ions. This type of tautomeric form in such compounds is already known. A search in the literature reveals that compound 3-phenyl-2-thio-2,4(1H, 3H)-quinazolinedione has been used for the complexation with Pb^{II} in solid state⁴. This clearly indicates that the complexation takes place through sulphur after the dissociation of a proton from -SH group. On these themes the present investigation of the stoichiometric metal-ligand stability constants of 3-methyl-2-thio-2,4(1H, 3H)-quinazolinedione with divalent metal ions and rare earth metal ions is reported for the first time.

Experimental

N(3)-Methyl derivative of 2-thio-2,4(1H, 3H)-quinazolinedione was prepared by standard

methods^{1,2}. The metal ions used were taken in the form of metal perchlorates, prepared from metal carbonates or oxides of A.R. grade. All these were estimated by EDTA titrations³. As the ligand was sparingly soluble in water, a medium consisting of 3 : 1 (v/v) dioxan-water was used in the present investigation. Potentiometric readings were taken on Toshniwal CL 46 digital pH meter having accuracy 0.01 with combined glass-calomel electrodes assembly at 27 ± 0.1°. The titrations were carried out in nitrogen atmosphere. The free acid, the free acid plus the ligand, and the mixture of acid, ligand and metal ion were titrated separately against carbonate free standard sodium hydroxide (1.105 M). Sodium perchlorate (0.1 M) was added to maintain the ionic strength constant.

Results and Discussion

\bar{n}_A values were obtained by using Irving and Rossotti equations and then pK value for the reagent was calculated. This value was also confirmed by the plots of (i) pH vs \bar{n}_A and (ii) pH vs $\log \bar{n}_A / 1 - \bar{n}_A$. These plots are shown in Fig. 1, and the mean value is recorded in Table 1.

The experimental readings are used to calculate the values of \bar{n} (average number of ligand molecules attached per metal ion) and pL (free ligand exponent) applying Irving and Rossotti method⁵. The \bar{n} values were plotted against the corresponding pL values to get the formation curves of the metal complexation equilibria (Fig. 2 and Fig. 3). These formation curves were used to determine $\log K_1$ and $\log K_2$ by half-integral method. The curves obtained were fairly symmetrical in nature in all the cases. In some cases $\log K_2$ values were

[†] Paper presented at the Annual Convention of Chemists, Madras, 1981.

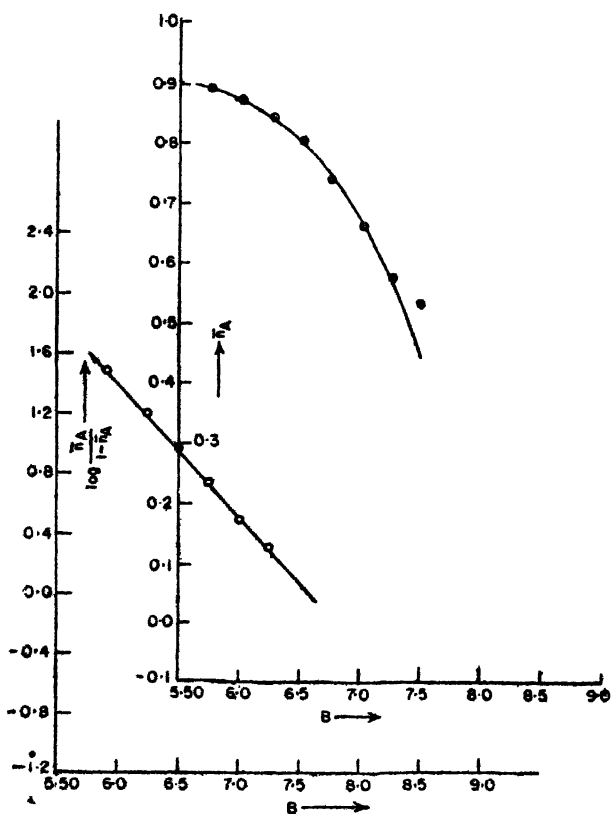


Fig. 1. Graph of B against $\log \frac{\bar{n}_A}{1 - \bar{n}_A}$;

Graph of B against \bar{n}_A .

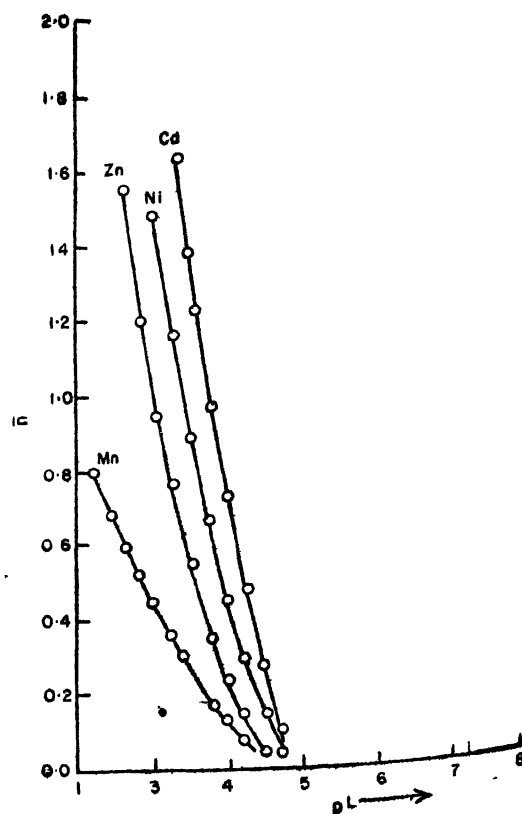


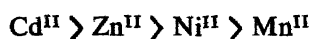
Fig. 2. Graph of \bar{n} against pL .

TABLE 1—STEPWISE STABILITY CONSTANTS OF COMPLEXES

Temp. = $27 \pm 0.1^\circ$, $\mu = 0.1 M$

H ⁺	Cd ^{II}	Zn ^{II}	Ni ^{II}	Mn ^{II}	Nd ^{III}	Sm ^{III}	Gd ^{III}	Dy ^{III}	
log K ₁	10.95	7.64	6.70	6.01	4.75	8.65	8.66	8.64	9.59
log K ₂	—	7.22	6.25	5.64	3.79	7.52	7.60	7.24	7.93

obtained by extrapolating the graphs. Limits of error and the standard deviation for K values were applied and the most representative values are recorded in Table 1. The order of stability constants in case of divalent metal ions studied was found to be



The order $Cd^{II} > Zn^{II}$ observed in the complexes in the present investigation is also in agreement with the observations made earlier with a few exceptions^{6,7}. This observation is in agreement with expectations based on the increase in both the ionisation potential and the reciprocal ionic radius on passing from cadmium to zinc. The order $Zn^{II} > Ni^{II}$ in case of ligands containing sulphur has been reported by many workers⁸⁻¹⁰.

With the contribution of electrons from the ligand, a strong covalent bond between metal ion and ligand is expected from nickel and manganese.

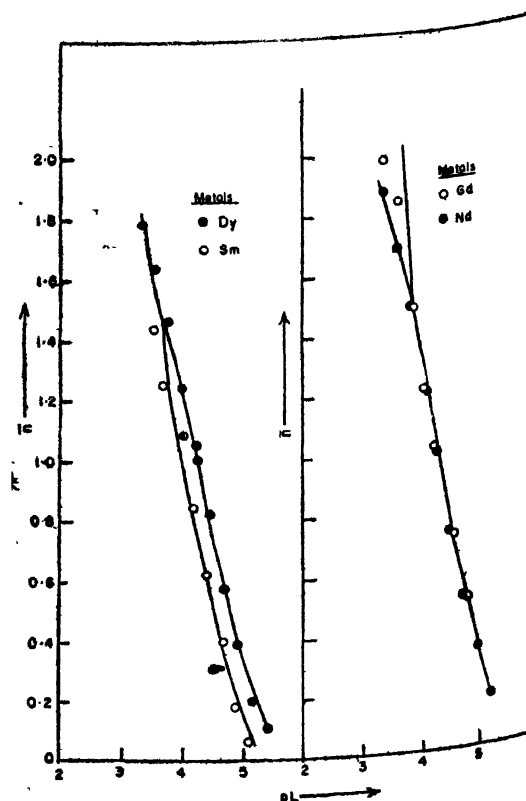


Fig. 3. Graph of \bar{n} against pL .

However, the observed stability order indicates that cadmium and zinc form stronger complexes than nickel and manganese. This is because the metal-ligand bond in case of cadmium and zinc is more of π type of bond with the back donation of electrons from these metal ions to the ligand. The observed stability order of cadmium complex as compared to zinc complex supports this explanation.

Only four rare earth metal ions have been studied for their complexation with the ligand. When their stability constants were compared with the divalent metal ions, it is observed that their values are higher. This indicates more ionic character of these rare-earth metal ion complexes. In order to have the detailed stability order, the study of the whole series of lanthanides is under investigation.

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