

Potentiometric Studies on the Complexes of Some Transition Metal Ions and Rare-Earth Ions with 3-Phenyl-2-thio-2,4, (1H, 3H) quinazolinedione

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Complexation equilibrium of metal complexes of Cu^{II} , Zn^{II} , Cd^{II} , Ni^{II} , Mn^{II} and rare-earth metals like Nd^{III} , Sm^{III} , Gd^{III} and Dy^{III} with 3-phenyl-2-thio-2,4, (1H, 3H) quinazolinedione have been studied potentiometrically. The proton dissociation constant of the reagent and the dissociation constant of its metal complexes have been determined by Calvin pH titration technique as adopted by Irving and Rossotti at $27 \pm 0.1^\circ$ and at ionic strength, $\mu = 0.1M$ in 3 : 1 (v/v) dioxane-water medium. The order of stability constants of the complexes is found to be $\text{Cu}^{II} > \text{Cd}^{II} > \text{Ni}^{II} > \text{Zn}^{II} > \text{Mn}^{II}$. The stability constants in case of rare-earth metal ions have been investigated only to know their ionic character.

2-THIO-2,4, (1H, 3H) quinazolinedione and its substituted derivatives are heterocyclic compounds having allied structures with those of thioxoimidazolidinones (2-thiohydantoin). In the present investigation the compound is prepared with the idea to use it as complexing agent. In the ligand molecule proton dissociation takes place because of the presence of tautomeric form of the ligand, giving rise to thiol group and thus the complexation with metal ion is possible. This type of tautomeric form in such compounds is already reported in the literature by ir spectral studies.

Experimental

The ligand 3-phenyl-2-thio-2, 4, (1H, 3H) quinazolinedione was synthesised by standard methods^{1,2} and recrystallized from acetic acid yielded colourless plates, m.p. 301° . The structure of the ligand molecule is confirmed by ir spectral analysis. Dioxan used was purified by standard method³. Distilled water was used throughout the investigation.

The free acid, free acid plus ligand and the mixture of metal containing the ligand and the acid were titrated against standard carbonate-free sodium hydroxide (0.1M). The solutions of metal perchlorates were prepared from A.R. grade oxide and carbonate, and standardised by EDTA titrations⁴. The potentiometric titrations were carried out in an inert atmosphere by bubbling oxygen-free nitrogen gas through the solution. All the measurements were carried out at $27 \pm 0.1^\circ$ in 3 : 1 (v/v) dioxane-water medium.

Results and Discussion

\bar{n}_A values were obtained by using Irving and Rossotti equation and then pK value for reagent

calculated. This value is confirmed by plot of pH vs \bar{n}_A and pH vs $\log \bar{n}_A/(1-\bar{n}_A)$ as shown in Fig. 1.

3-Phenyl-2-thio-2,4, (1H, 3H) quinazolinedione has been reported for the complexation with Pb^{II} in solid state⁵. This clearly indicates that the complexation has taken place through sulphur after the dissociation of proton from SH group. On this basis the present investigation of the stoichiometric metal-ligand stability constant of 3-phenyl-2-thio-

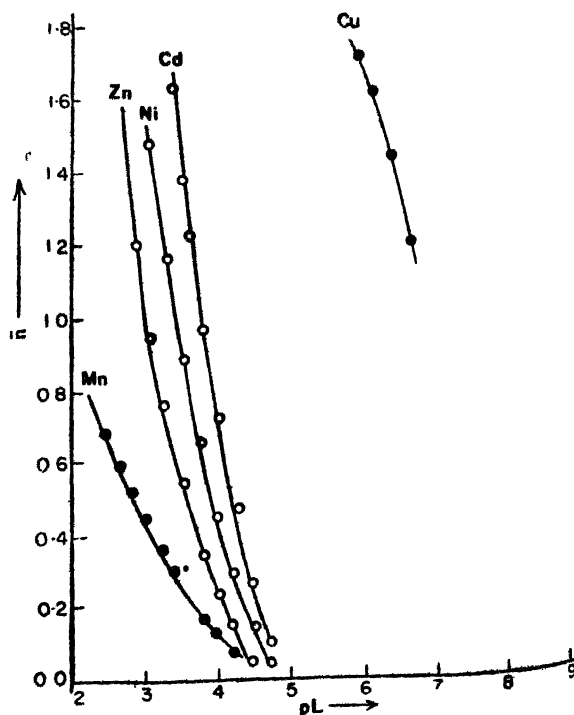


Fig. 1

*Part of the paper presented at the Annual Convention of Chemists, Madras, 29th December, 1981.

TABLE 1—STEPWISE STABILITY CONSTANTS OF VARIOUS COMPLEXES

Temp. = 27 ± 0.1°		$\mu = 0.1 M$								
	H ⁺	Cu ^{II}	Cd ^{II}	Ni ^{II}	Zn ^{II}	Mn ^{II}	Sm ^{III}	Gd ^{III}	Dy ^{III}	Nd ^{III}
log K ₁	7.54	—	4.20	3.93	3.55	2.90	4.60	4.75	4.80	4.85
log K ₂	—	6.22	3.55	2.90	2.65	—	3.65	3.71	3.65	3.85

2,4, (1*H*, 3*H*) quinazolinedione with transition metal ions and rare-earth metal ions is reported for the first time.

The value of \bar{n} (average number of ligand molecule attached per metal ion) and pL (free ligand exponents) were calculated applying Irving and Rossotti method⁶. The plot of \bar{n} vs pL gave the formation curve of metal complexation equilibria (Fig. 2).

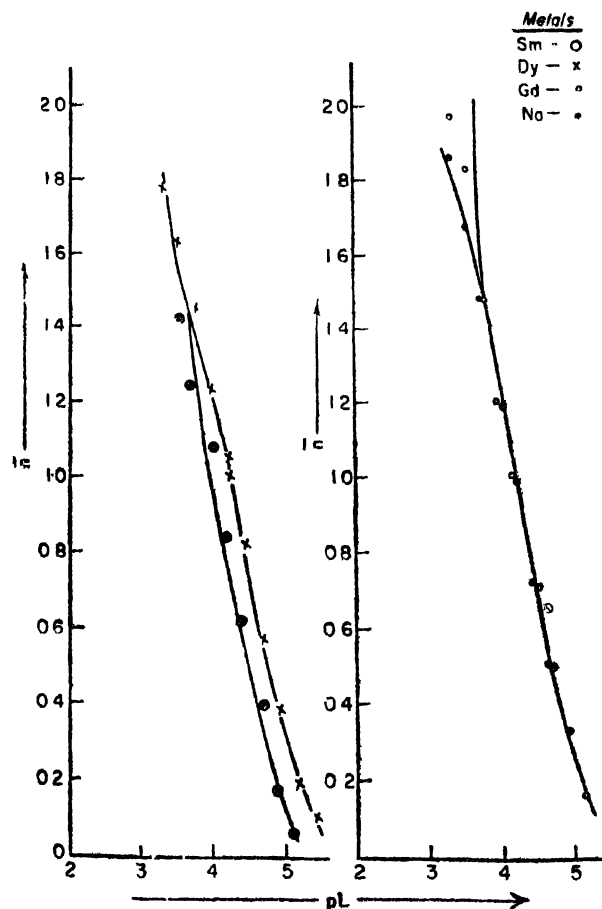


Fig. 2. Graph of \bar{n} against pL .

The formation curves were used to determine log K₁ and log K₂ by half integral method. The curves obtained are fairly symmetrical in nature in all the cases. In some cases log K₂ values were obtained by extrapolation. Where the difference between log K₁ and K₂ found to be less than 1.78 units, the same were calculated by least square method. Cu^{II} is noticed to form only 1 : 2 complexes. The non-existence of 1 : 1 complex with this metal may be due to the absence of stepwise formation of complex. It is also observed that log K₂ value with this metal ion is very high, which again indicates greater stability of 1 : 2 complex. Limits of error and the standard deviations for log K values are applied and most representative values are recorded in Table 1. The order of stability constant for transition metals is found to be Cu^{II} > Cd^{II} > Ni^{II} > Zn^{II} > Mn^{II}. This order of stability is in agreement with the order reported earlier.

As regards to the stability order of complexes for rare-earth metals, it is expected to get a gradual increase in stability with increase in atomic number because of the well known lanthanide contraction. However, it is verified with a few rare-earth metal ions and their values are reported in Table 1.

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