Metal ion	$1/r$ (Å⁻¹)	$\log K_1$	$\log K_2$	$\log K_3$	$\log \beta_3$
La³⁺	0·942	4·33	3·95	3·25	11·53
Ce³⁺	0·967	4·54	4·25	4·11	12·90
Pr³⁺	0·987	4·75	4·39	4·33	13·47
Nd³⁺	1·005	4·88	4·51	4·43	13·82
Sm³⁺	1·037	5·25	4·29	4·20	13·74
Eu³⁺	1·052	5·16	4·44	4·32	13·92
Gd³⁺	1·066	4·99	3·90	3·67	12·56
Dy³⁺	1·101	5·04	4·11	4·05	13·20
Ho³⁺	1·118	5·11	4·25	4·10	13·46
Er³⁺	1·135	5·29	4·29	4·15	13·73
Yb³⁺	1·165	5·35	4·32	4·18	13·85
Y³⁺	1·136	4·83	3·95	3·84	12·62

on the accuracy of the earlier constants and there will be accumulation of error in the successive steps.

The practical acid dissociation constant ($pK_a = 9\cdot34$) of HSDBM as determined by us is in excellent agreement with value ($pK_a = 9\cdot38$) reported by Manone and Saito[11] in 3:1 dioxane-water mixture at an ionic strength of 0·1. Uhlemann et al.[12] reported the thermodynamic acid dissociation constant, pK_D of HSDBM in 75% aqueous dioxane, and their value $pK_D = 11\cdot40$ is somewhat higher than the value $pK_D = 11\cdot14$, reported by Chaston et al.[13]. Fernelius and his coworkers[14] have observed that dibenzoylmethane form relatively strong complex with Na⁺, so its monothio analogue may also show a similar trend. Since we were primarily interested in the evaluation of practical stability constants of lanthanide-HSDBM complexes, no attempt was made to determine the thermodynamic acid dissociation constant.

Table 1 shows the first three formation constants of eleven lanthanide and yttrium ions. In general, for a given metal ion, $\log K_1 > \log K_2 > \log K_3$. However, the difference between any two consecutive constants is quite small, indicating that there is an almost equal tendency for all of the complex species to coexist in solution. It seems probable that when $\bar{n} > 2$, the concentration of the tetrakis-complex $[LnA_4]^-$ in the equilibrium system becomes appreciable. In fact, both the tris- and the tetrakis-complexes of HSDBM have been isolated by us[8].

The formation constants of 1:1 complexes exhibit the trend commonly observed in various complexes of lanthanides[15,16]. It is apparent from Table 1 that the $\log K_1$ values monotonically increase from La(III) to Sm(III) with respect to the $1/r$ values (where r stands for ionic radius). The middle portion of the series show a decline with the Gd(III) value at the minimum. After Gd(III), there is slow increase in $\log K_1$ and the value of Sm(III) is almost equal to that of Er(III). It may also be noted that $\log K_1$ of Y(III) falls in between those of Pr(III) to Nd(III). The change in aquoion structure and depression of class-b character in the middle of the lanthanide series appear to govern the sequence of formation constants throughout the series[17].

The lower stabilities of thio-β-diketonates in comparison with β-diketonate[1] impose greater Lewis acidity or residual coordinating power in the complexes. This has been verified[6] by measuring

the formation constants of the mixed complexes of Nd(STTA)₃ with several neutral donors which are found to have greater values than those of the Nd(TTA)₃ adducts. Thus it is expected that the lanthanide monothio-β-diketonates might serve as better shift reagents than the currently popular β-diketonates. Work with suitable reagents in this direction is in progress.

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Influence of Concentration & Nature of Supporting Electrolytes on the Kinetics of Reduction of Zn(II) at Dropping Mercury Electrode

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The polarographic behaviour of Zn(II) has been studied in a variety of supporting electrolytes of varying concentrations, viz. NaCl, NaClO₄, NaNO₃, KCl, KClO₄, KNO₃, KNO₂, KBr, KI, K₂SO₄, KH₂PO₄, KCNS, pot. acetate, pot. oxalate, pot. tartrate, pot. citrate, pot. benzoate, NH₄Cl, NH₄NO₃, Mg(NO₃)₂, Ca(NO₃)₂, Sr(NO₃)₂ and Ba(NO₃)₂. It has been found that the reduction of Zn(II) at d.m.e. in the presence of pot. oxalate, pot. citrate and 0·5M pot. tartrate is totally irreversible while in other supporting electrolytes it is quasi-reversible. The kinetic parameters, viz. the transfer coefficient (α) and standard rate constant ($k_{s,h}$) of the quasi-reversible electrode process have been calculated by Gellings' method. The influence of concentration and nature of supporting electrolytes on the kinetics of quasi-reversible electrode process of Zn(II) has been discussed in terms of the values of $k_{s,h}$ and 'α'.

THE nature of the reduction of Zn(II) at d.m.e. is still regarded a vexed problem inasmuch as that many polarographic studies, under somewhat similar conditions, do not unambiguosly illustrate if the reduction is reversible, quasi-reversible or irreversible in the same supporting electrolyte[1]. This behaviour has also been observed in fluoride supporting electrolytes[2-4]. According to Bond[1] the conflicting results obtained by various workers on the polarographic behaviour of Zn(II) could be caused by differences in supporting electrolyte or drop time, or the presence or absence of a particular surface-active maximum suppressor.

Mukherjee and Chakravarti[5], and Nath and Bhattacharya[6] have studied the influence of the nature and concentration of some supporting electrolytes on $E_{1/2}$ and i_d of Zn(II). While Mukherjee and Chakravarti held that viscosity and complex formation are the two important parameters which affect $E_{1/2}$ and i_d, Nath and Bhattacharya emphasized the role of adsorption at the mercury-solution interface in affecting $E_{1/2}$ and i_d.

From a survey of the literature[1-4,7-9] it is evident that much remains to be investigated with regard to the nature of the electrode reaction of Zn(II) at d.m.e. in a variety of supporting electrolytes particularly in complexing supporting electrolytes. With this aim in view, the present study dealing with the polarographic behaviour of Zn(II) in complexing and non-complexing supporting electrolytes of varying concentrations has been undertaken.

ZnCl$_2$ and the supporting electrolytes were either of AR (BDH) or GR (E. Merck) grade. Their stock solutions were prepared in conductivity water. The resultant concentration of Zn(II) was maintained at $1.0 \times 10^{-3} M$ in each case.

A manual polarograph (Toshniwal, CLO2) in conjunction with a polyflex galvanometer (Toshniwal, PL50) was used. The d.m.e., used in conjunction with SCE, had the following characteristics: $h_{corr} = 61.32$ cm, $m = 2.075$ mg/sec, $t = 3.45$ sec (in $0.1M$ KCl, open circuit); and $m^{2/3}t^{1/6} = 2.005$ mg$^{2/3}$ sec$^{-1/2}$.

All the measurements were made at $25° \pm 0.1°$. Purified hydrogen was used for removing dissolved oxygen. Since no maxima appeared in the case of Zn(II) in the present study, addition of a suppressor was avoided.

Zn(II) gives a single well-defined wave in each of the supporting electrolytes of varying concentrations. The limiting current is diffusion-controlled in each case as evidenced by the linearity of i_d vs $\sqrt{h}$ plots. The plots of $E_{d.e.}$ vs log $i/(i_d - i)$ are linear in all the cases (representative Fig. 1).

Applying different criteria[10,11] of reversibility and irreversibility of the electrode process, it has been found that the reduction of Zn(II) in potassium oxalate, potassium citrate and in $0.5M$ potassium tartrate is totally irreversible while in other supporting electrolytes used in the present study, reduction is neither totally irreversibile nor does it fulfil the requirements of reversibility. The slope values of log plots in these cases lie in the range 0.040-0.050 V (Table 1). These slope values suggest[8]
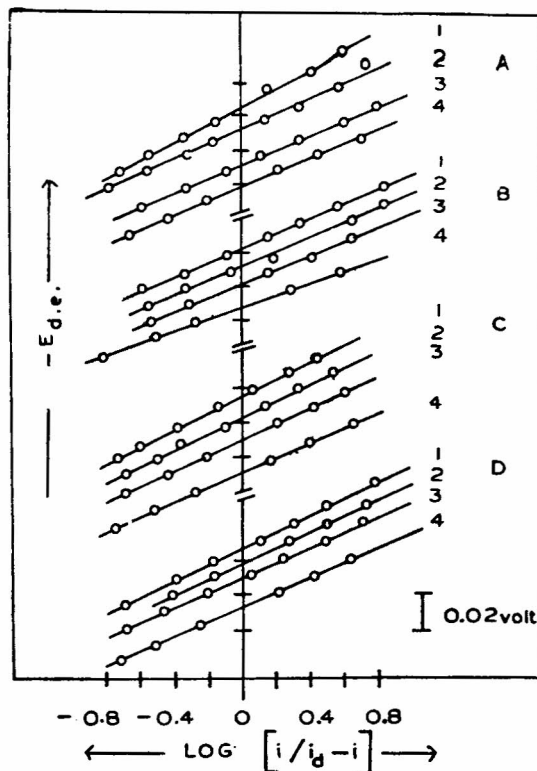
Fig. 1 — Log plots of Zn(II) in (1) $1M$, (2) $M/2$, (3) $M/10$ and (4) $M/20$ concentration of supporting electrolytes (A) Ba(NO$_3$)$_2$, (B) Sr(NO$_3$)$_2$, (C) Ca(NO$_3$)$_2$ and (D) Mg(NO$_3$)$_2$

the quasi-reversible nature of the electrode process of Zn(II) at d.m.e.

Gellings' method[12] as also used by Gaur and coworkers[8] has been used to evaluate $E_{1/2}^r$ (the reversible half-wave potential) and the kinetic parameters ('α' and $k_{s,h}$) of the quasi-reversible electrode process.

The calculated values of $k_{s,h}$ are listed in Table 1. These values are of the same order of magnitude as suggested by Delahay[13] for quasi-reversible electrode processes. Thus, except for potassium oxalate, potassium citrate and $0.5M$ potassium tartrate, the quasi-reversible nature of the polarographic reduction of Zn(II) in all the other supporting electrolytes used in this study is ascertained.

It is also evident that the value of the standard rate constant ($k_{s,h}$) for the electrode reaction of Zn(II) at d.m.e. decreases with an increase in [supporting electrolyte] in all the cases (Table 1). This suggests that with increase in [supporting electrolyte] the electrode reaction is gradually pushed towards irreversibility. This may be due to the increased adsorption of the ions of the supporting electrolytes on the electrode surface at higher concentrations[14]. A decrease in the value of 'α' with an increase in [supporting electrolyte] lends further support to this conclusion[15].

Taking different sets of supporting electrolytes such that when cation was varied anion remained identical and vice versa, the effect of anions and cations at a certain concentration ($0.1M$) on the value of $k_{s,h}$ has been attempted.

TABLE 1 — VALUES OF POLAROGRAPHIC AND KINETIC PARAMETERS FOR THE REDUCTION OF Zn(II) IN DIFFERENT SUPPORTING ELECTROLYTES

[Supporting electrolyte]	Slope V	$-E'_{1/2}$ V (SCE)	α	$k_{s,h} \times 10^3$ cm/sec
NaCl				
M/20	0.0420	0.987	0.37	6.40
M/10	0.0500	0.988	0.36	5.56
M/2	0.0526	0.986	0.35	5.32
M	0.0542	0.995	0.34	4.45
NaClO$_4$				
M/20	0.0373	0.974	0.44	6.42
M/10	0.0384	0.973	0.43	6.08
M/2	0.0408	0.973	0.42	5.82
M	0.0555	0.974	0.41	5.24
NaNO$_3$				
M/20	0.0510	0.958	0.47	6.40
M/10	0.0501	0.970	0.46	6.16
M/2	0.0520	1.001	0.44	4.56
M	0.0490	1.002	0.44	4.20
KCl				
M/20	0.0500	0.987	0.44	7.94
M/10	0.0444	0.991	0.41	6.60
M/2	0.0416	0.997	0.40	6.08
M	0.0454	1.013	0.37	4.36
KClO$_4$				
M/40	0.0400	0.975	0.38	8.12
M/30	0.0434	0.978	0.37	8.07
M/20	0.0454	0.976	0.36	7.68
M/10	0.0465	0.977	0.34	7.32
KNO$_3$				
M/20	0.0435	0.962	0.41	7.28
M/10	0.0444	0.987	0.40	6.60
M/2	0.0512	0.996	0.39	6.40
M	0.0521	1.000	0.38	5.92
KNO$_2$				
M/20	0.0424	1.030	0.36	5.68
M/10	0.0488	1.028	0.35	5.11
M/2	0.0500	1.039	0.34	4.36
M	0.0555	1.056	0.35	4.36
KBr				
M/20	0.0370	1.012	0.34	7.28
M/10	0.0380	1.018	0.33	6.32
M/2	0.0400	1.028	0.32	5.00
M	0.0440	1.025	0.30	3.60
KI				
M/20	0.0384	1.018	0.32	5.80
M/10	0.0400	1.014	0.32	5.48
M/5	0.0416	1.025	0.31	5.16
M/2	0.0434	1.023	0.30	4.84
K$_2$SO$_4$				
M/20	0.0434	1.024	0.35	6.52
M/10	0.0440	1.028	0.34	5.38
M/5	0.0454	1.029	0.33	5.06
M/2	0.0459	1.035	0.32	4.85

[Supporting electrolyte]	Slope V	$-E'_{1/2}$ V (SCE)	α	$k_{s,h} \times 10^3$ cm/sec
KH$_2$PO$_4$				
M/20	0.0400	1.024	0.35	6.42
M/10	0.0440	1.037	0.34	5.04
M/5	0.0454	1.051	0.33	4.96
M/2	0.0500	1.068	0.33	4.56
POT. ACETATE				
M/20	0.0500	1.011	0.44	5.38
M/10	0.0525	1.030	0.43	5.15
M/2	0.0512	1.052	0.41	4.86
M	0.0470	1.066	0.40	4.25
POT. TARTRATE				
M/20	0.0512	1.052	0.47	4.68
M/10	0.0526	1.063	0.45	3.76
M/5	0.0555	—	—	—
M/2	0.0714	—	—	—
POT. BENZOATE				
M/40	0.0440	1.026	0.42	5.76
M/20	0.0454	1.034	0.41	5.42
M/10	0.0500	1.032	0.41	4.95
M/5	0.0512	1.030	0.40	4.32
KCNS				
M/20	0.0370	0.997	0.32	6.20
M/10	0.0408	1.012	0.31	6.04
M/2	0.0440	1.035	0.30	5.08
M	0.0465	1.033	0.30	4.53
NH$_4$Cl				
M/20	0.0434	0.979	0.37	6.84
M/10	0.0454	0.984	0.34	6.64
M/2	0.0487	1.022	0.32	5.84
M	0.0500	1.021	0.31	5.00
NH$_4$NO$_3$				
M/20	0.0374	0.988	0.33	5.48
M/10	0.0425	0.992	0.32	4.98
M/2	0.0444	0.997	0.31	4.78
M	0.0476	0.996	0.30	4.59
Mg(NO$_3$)$_2$				
M/20	0.0425	1.015	0.35	6.71
M/10	0.0434	1.014	0.34	6.19
M/2	0.0454	1.011	0.33	5.67
M	0.0500	0.998	0.32	4.48
Ca(NO$_3$)$_2$				
M/20	0.0454	1.014	0.43	8.88
M/10	0.0465	1.016	0.41	7.75
M/2	0.0476	1.021	0.40	7.35
M	0.0512	1.010	0.38	6.04
Sr(NO$_3$)$_2$				
M/20	0.0372	1.018	0.33	6.51
M/10	0.0408	1.099	0.32	6.25
M/2	0.0425	1.020	0.32	5.72
M	0.0440	1.020	0.31	5.44
Ba(NO$_3$)$_2$				
M/40	0.0416	1.005	0.34	6.14
M/20	0.0440	1.007	0.32	5.65
M/10	0.0454	1.016	0.31	5.24
M/5	0.0514	1.020	0.30	4.80

The order of $k_{s,h}$ value is as follows:
(i) For univalent cations (nitrates): $K^+ > Na^+ > NH_4^+$
(ii) For bivalent cations (nitrates): $Ca^{2+} > Sr^{2+} > Mg^{2+} > Ba^{2+}$
(iii) For anions (as potassium salts): $ClO_4^- > NO_3^- > Cl^- > Br^- > CNS^- > I^- > SO_4^{2-} > CH_3COO^- > NO_2^- > H_2PO_4^- > C_6H_5COO^- > tart^{2-}$

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Kinetics of the Reaction between Ferric Chloride & Thiourea

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Kinetics of the reaction between ferric chloride and thiourea have been studied at pH 1·5. The total order of reaction is found to be 1·5, one with respect to thiourea and 0·5 with respect to ferric chloride. The energy of activation, frequency factor and entropy of activation have been determined. Urea is found as one of the products of the reaction. A probable reaction mechanism has been proposed.

REDOX reactions of ferric chloride in acetone, with some compounds of thiourea type have been reported previously by Kovacovu[1]. However the reaction has not been studied in aqueous medium. The present paper reports the results of a systematic kinetic study of the reaction between ferric chloride and thiourea in water.

All the chemicals used were of CP grade and the solutions were prepared in doubly distilled water. Ferric chloride solution was standardized by potassium dichromate method. The pH of solutions were adjusted to 1·50.

The course of the reaction was followed at different time intervals by measuring the absorption at 420 nm employing an ERMA 600 photoelectric colorimeter. This wavelength gives the maximum absorption for ferric chloride.

It is observed that at constant [thiourea] the rate increases with increasing [$FeCl_3$] (Table 1). The order of reaction with respect to ferric chloride was determined using Vant Hoff differential equation taking concentration in terms of initial optical density. It is found that the order of reaction with respect to ferric chloride is 0·50. At constant [$FeCl_3$], the rate increases with increasing [thiourea] (Table 2). The plot of $\log x$ against $\log dx/dt$ is linear with a slope of unity indicating that the rate follows first order kinetics with respect to thiourea. Hence the total order of reaction with respect to ferric chloride and thiourea is 1·5.

It is observed that the rate constant increases as the ionic strength increases (Table 3), indicating

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TABLE 1 — EFFECT OF VARYING [$FeCl_3$] ON THE REACTION RATE

{$[CS(NH_2)_2] = 0.1 M$; temp. = 30°; $pH = 1.5$}

[$FeCl_3$] M	$-dx/dt \times 10^3$ min^{-1}	[$FeCl_3$] M	$-dx/dt \times 10^3$ min^{-1}
0·05	10·0	0·0125	6·4
0·0375	8·0	0·005	4·35
0·025	7·5	—	—

TABLE 2 — EFFECT OF VARYING [$CS(NH_2)_2$] ON THE REACTION RATE

[$FeCl_3 = 0.0375 M$; temp. = 30°; $pH = 1.5$]

[$CS(NH_2)_2$] M	$-dx/dt \times 10^2$ min^{-1}	$K_I \times 10^2$ min^{-1}	$K_{II} \times 10^2$ min^{-1}
0·05	1·3	1·363	1·69
0·1	3·0	3·60	4·30
0·15	6·9	5·71	9·60
0·20	10·0	10·5	18·0
0·25	12·4	14·0	28·0

K_I is the first order rate constant and K_{II} is 1·5 order rate constant.

TABLE 3 — EFFECT OF ADDED SALT ON REACTION RATE

[$FeCl_3 = 0.0375 M$; $CS(NH_2)_2 = 0.05 M$; temp. = 30°; $pH = 1.5$]

[NaCl] M	$K_{II} \times 10^2$ min^{-1}	[NaCl] M	$K_{II} \times 10^2$ min^{-1}
0·00	1·69	0·15	22·0
0·05	6·6	0·2	24·0

K_{II} is 1·5 order rate constant.

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