overnight, was filtered and recrystallized from methanol, m p. 118–20°, yield 50%, Found N, 15.92; $C_{16}H_{20}N_4O_2S$ requires N, 16.18%, . IR: 3480 (OH), 3240 (NH), 2970 & 2875 (CH), 1725 (C = O), 1625 (C = N), 1180 (C = S).

1-Substituted aminomethyl-3-cyclohexylthiosemicarbazono-2-indolinones (IV):

Method A

An appropriate 3-cyclohexylthiosemicarbazono-2-indolinone (I, 0.005 mol) was suspended in 10 ml of warm ethanol. To this suspension was added 1 ml of 37% formalin and an appropriate secondary amine (0.005 mol) with vigorous stirring. This mixture was then heated on a water bath for 10 min and allowed to remain at room temperature overnight. The separated solid product was filtered, washed with petroleum ether (b.p. 60–80°) and finally recrystallized from ethylacetate/chloroform-petroleum ether (b.p. 60–80°). All compounds (IV) thus synthesized are listed in table 1, yield 55–70%. Their IR spectra showed characteristic absorption bands at 3300–3225 (NH), 2900–2870 and 2825–2800 (CH), 1685–1670 (C = O), 1615–1600 (C = N), 1185–1150 (C = S). PMR ($CdCl_3$) of IV_g: 1.13–2.30 (*m*, 11H, CH_2, *CH*), 2.38 (*s*, 3H, CH_3), 2.47–2.74 (*m*, 4H, CH_2-N–CH_2), 3.54–3.84 (*m*, 4H, CH_2-O–CH_2), 4.45 (*s*, 2H, N-CH_2-N), 7.05 (*q*, J=9 & 1.5 Hz, 1H, H_b), 7.40 (*d*, J=1Hz, 1H, *H*a), 7.64 (*d*, J = 6.5 Hz, 1H, *H*c); PMR ($CdCl_3$) of IV_j: 1.17–2.07 (*m*, 11H, CH_2, *CH*), 2.14 (*s*, 3H, Ar-CH_3), 2.25 (*s*, 3H, N-CH_3), 2.26–2.65 (*m*, 8H, CH_2-N-CH_2), 4.36 (*s*, 2H, N-CH_2-N), 6.88 (*q*, J = 9 & 1.5 Hz, 1H, *H*b), 7.30 (*d*, J = 1 Hz, 1H, *H*a), 7.55 (*d*, J = 4.5 Hz, 1H, H_c); PMR ($CdCl_3$) of IV_n: 1.02–2.30 (*m*, 17H, *CH*, *CH*), 2.37–2.74 (*m*, 4H, CH_2-N-CH_2), 4.43 (*s*, 2H, N-CH_2-N), 6.97 (*d*, J = 7.5 Hz, 1H, *H*c), 7.31 (*q*, J = 9 & 1.5 Hz, 1H, *H*b), 7.52 (*d*, J = 2 Hz, 1H, *H*a).

Method B

1-Morpholinomethyl-3-cyclohexylthiosemicarbazono-2-indolinone (IVa), prepared according to the method A, was also prepared by heating a mixture of 1-hydroxymethyl-3-cyclohexylthiosemicarbazono-2-indolinone (III, 0.005 mol) and morpholine (0.005 mol) in 10 ml ethanol, on a water bath for 10 min. The mixture was stirred vigorously and allowed to stand overnight. The separated solid was filtered, washed with petroleum ether (b.p. 60–80°) and recrystallized from ethylacetate. This compound was identical with the compound IVa synthesized by method A. PMR ($CdCl_3$) spectrum of this compound exhibited signals at 1.10–2.24 (*m*, 11H, CH_2, *CH*), 2.36–2.67 (*m*, 4H, CH_2-N-CH_2), 3.38–3.74 (*m*, 4H, CH_2-O-CH_2), 4.36 (*s*, 2H, N-CH_2-N), 6.94–7.68 (*m*, 4*H*, Ar-*H*).

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KINETICS OF POLYMERIZATION OF ACRYLAMIDE INITIATED BY Mn^{3+}- L-THREONINE REDOX SYSTEM

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MANGANESE (III) salts in combination with a variety of reducing agents such as diglycolic acid[1], isobutyric acid[2], ascorbic acid[3], thioglycolic acid[4], ethoxyacetic acid[5], etc. have been used for polymerization of vinyl monomers. In this paper, we report the kinetics of polymerization of acrylamide (AAM) initiated by Mn^{3+}-L-Threonine (L-TRN) redox system.

Acrylamide was purified by recrystallization from chloroform. Manganese (III) acetate dihydrate was prepared by a known method[6]. Sodium bisulphate. L-Threonine and all other chemicals used were of analar grade. Polymerization was carried out in nitrogen atmosphere in polymerization tubes. All the experiments were conducted in aqueous sulphuric acid medium. R_p was followed by bromometry and $-R_m$ by iodometry.

Polymerization of AAM initiated by Mn^{3+}-L-TRN system takes place at measurable rates at 40°C. The steady state is attained in 5 min. The rate of polymerization increases [(2.94–20.27) × 10^{-5} m.1^{-1} .s^{-1}] with increasing [AAM] (0.1028–0.7199 M). The plot of log R_p vs log [AAM] is a straight line with unit slope (figure 1A) and the plot of R_p vs [AAM] is a straight line (figure 1B) showing that the order with respect to [AAM] is one. R_p is found to be independent of [Mn^{3+}], [L-TRN], [H^+] and ionic strength.

Rate of Mn^{3+}-ion disappearance ($-R_m$) increases [(0.9–3.1) × 10^{-6} m.1^{-1} .s^{-1}] with increasing [Mn^{3+}] [(0.909–5.909) × 10^{-3} M]. The plot of $-R_m$ vs [Mn^{3+}] is a straight line with zero intercept (figure 2A) showing the first order dependence of $-R_m$ on [Mn^{3+}]. $-R_m$ also increases linearly with the increase of [L-TRN]. The plot of $(-R_m)^{-1}$ vs $[\text{L-TRN}]^{-1}$ is a straight line with an intercept on the $(-R_m)^{-1}$ axis (figure 2B). This indicates the formation of a weak complex between Mn^{3+} and L-TRN. Similar observations have been made by Santappa *et al*[2]. $-R_m$ is found to be independent of [AAM], [H^+] and ionic strength. R_p is decreased slightly by the addition of water miscible organic solvents such as acetone and ethanol. $-R_m$ is not affected by the addition of such solvents.

To explain these experimental observations the following kinetic scheme is proposed:

$$Mn^{3+} + \text{L-TRN} \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} \text{complex}$$

$$\xrightarrow[\text{slow}]{k_d} R^{\cdot} + Mn^{2+} + H^{+}$$

$$R^{\cdot} + Mn^{3+} \xrightarrow{k_0} \text{products}$$

$$R^{\cdot} + M \xrightarrow{k_i} M^{\cdot}$$

$$M^{\cdot} + M \xrightarrow{k_p} M_1^{\cdot}$$

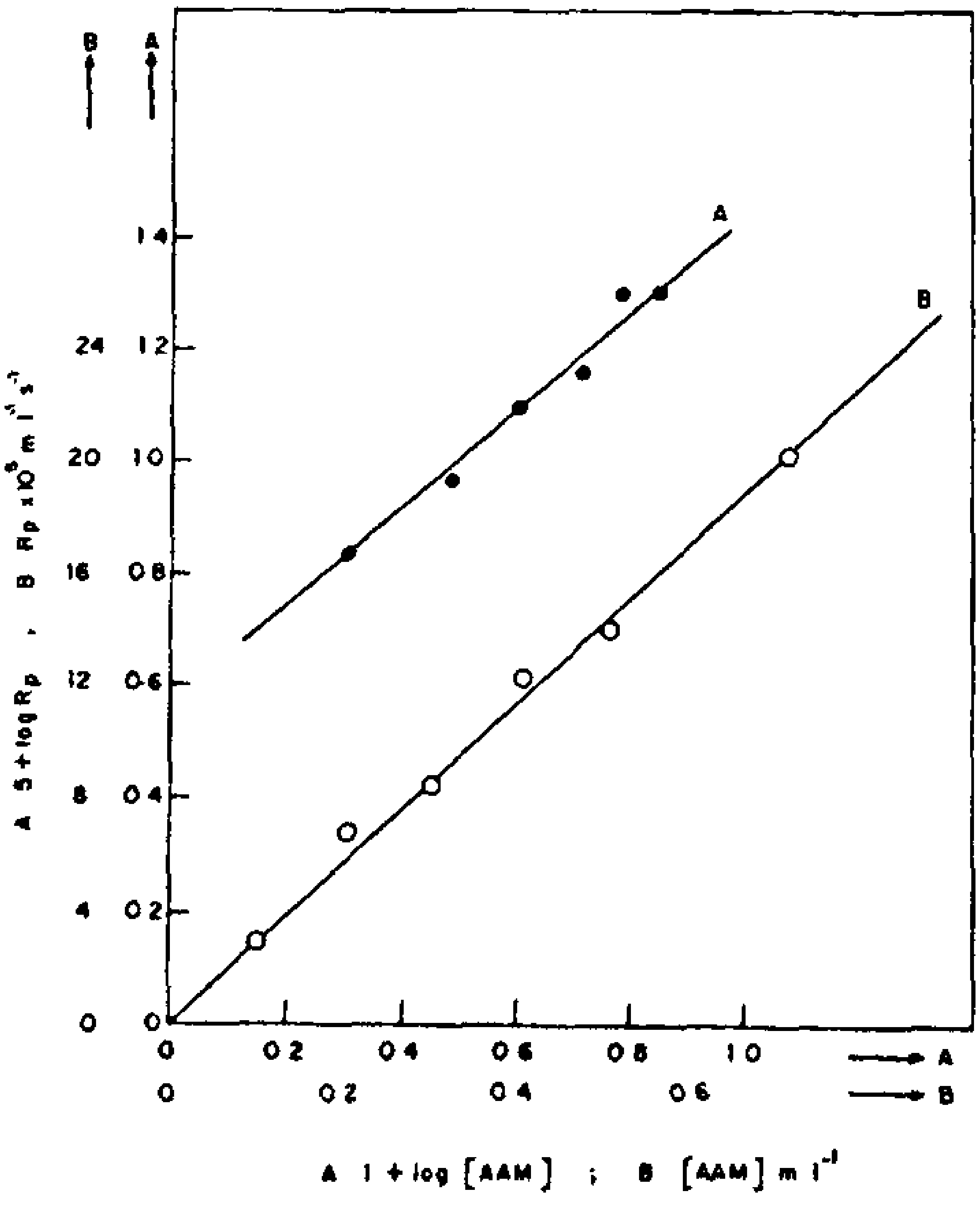

Figure 1. Variation of R_p with [AAM].

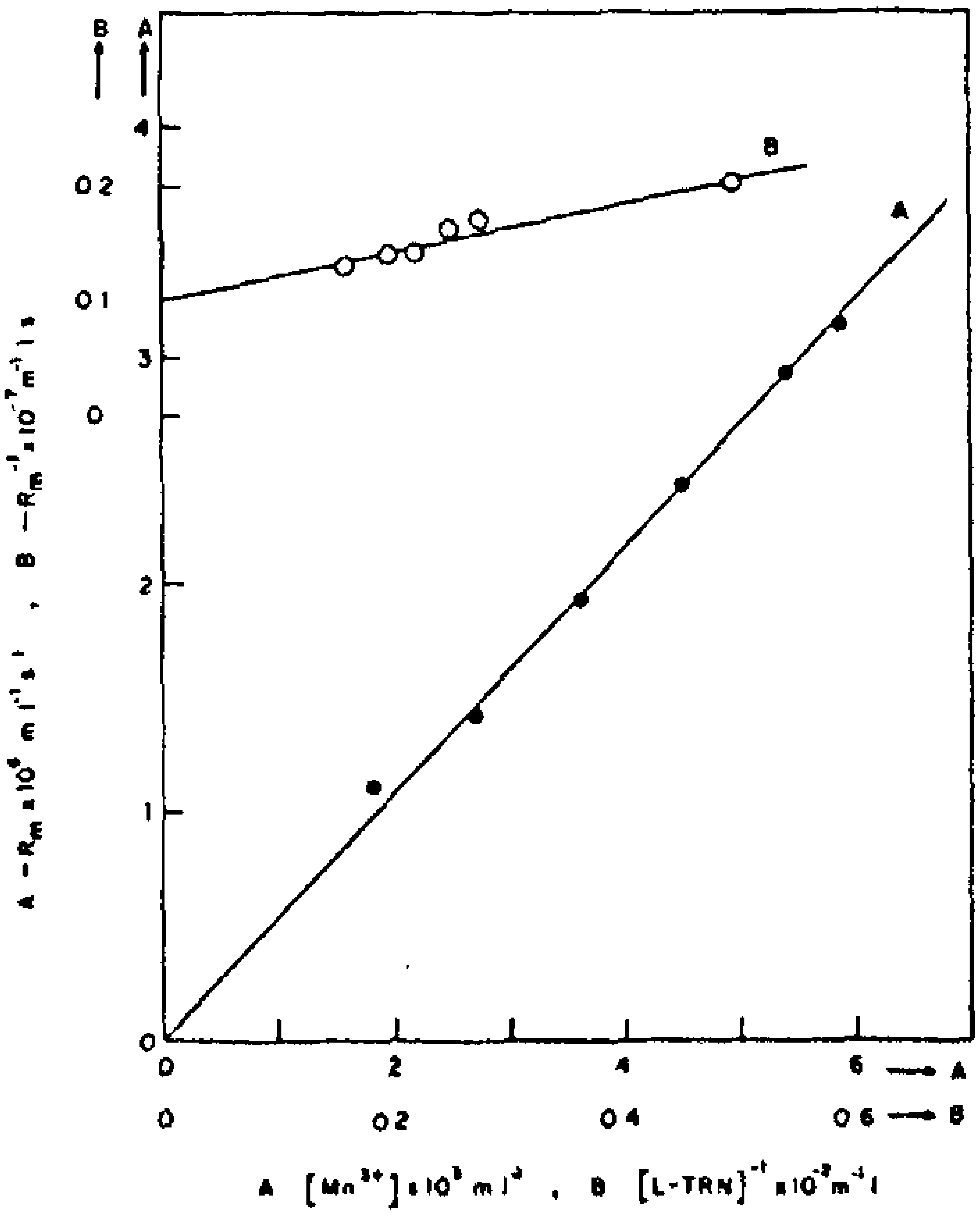

Figure 2. Variation of $-R_m$ with [Mn^{3+}] and [L-TRN].

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$$M^{\cdot}_{x-1} + M \xrightarrow{k_p} M^{\cdot}_x$$

$$M^{\cdot}_x + \text{complex} \xrightarrow{k_t} \text{polymer} + \text{Mn}^{2+} + \text{Z}$$

where Z may be L-TRN itself or an inactive product obtained from L-TRN (M = AAM). Using the steady-state assumption, the following expressions are derived

$$R_p = \frac{k_p \cdot k_d\,[\text{AAM}]^2}{k_t\,([\text{AAM}] + (k_o/k_t)\,[\text{Mn}^{3+}])} \cdot \qquad (1)$$

The value of the term (k_o/k_t) $[\text{Mn}^{3+}]$ is negligibly small (0.0177) when compared to the value of [AAM]. Hence neglecting (k_o/k_t) $[\text{Mn}^{3+}]$ in (1), the following equation is obtained

$$R_p = (k_p \cdot k_d\,[\text{AAM}])/k_t\,. \qquad (2)$$

$-R_m$ is given by the expression

$$-R_m = \frac{2Kk_d\,[\text{Mn}^{3+}]_{\text{total}}\,[\text{L-TRN}]}{1 + \text{K}\,[\text{L-TRN}]}, \qquad (3)$$

where $[\text{Mn}^{3+}]_{\text{total}} = [\text{Mn}^{3+}] + \text{K}\,[\text{Mn}^{3+}]\,[\text{L-TRN}]$.

The expressions (2) and (3) agree with our observations. Various kinetic and thermodynamic parameters have been evaluated and presented:

$\Delta E_a^{\neq}$ k cal.mol^{-1}	$\Delta S^{\neq}_{313\,^\circ\text{K}}$ e.u. mol^{-1}	$\Delta G^{\neq}$ k cal. mol^{-1}	k_p/k_t	k_o/k_t
3.32	−67.30	24.39	0.9966	6.731

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A NEW ISOLATE OF *PLASMODIUM FALCIPARUM* AND ITS CHLOROQUINE SENSITIVITY

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MALARIA caused by the protozoan parasites of genus *Plasmodium* has been identified as a major public health problem in many developing countries including India[1]. Falciparum malaria due to *P. falciparum* is the most fatal form of the disease and also involves cerebral, renal and pulmonary complications. Although the overall incidence of malaria, after an upsurge in 1970's, has shown a decreasing trend in recent years (2 million cases in 1984), the incidence of *P. falciparum* has proved less responsive and constitutes a higher proportion of the total malaria cases (30% in 1984 as compared to 10% in 1977)[2].

The chloroquine-resistant strain of *P. falciparum* has emerged as the major setback to chemotherapy necessitating major international efforts. But the mechanism of antimalarial drug action as well as biochemical and genetic mechanisms of resistance are not known[3,4]. Studies on different geographical isolates of *P. falciparum* and their drug sensitivity are essential to understand the mechanism and spread of drug resistance as well as to evolve suitable chemotherapeutic measures. Studies on different isolates of *P. falciparum* outside India have shown the existence of genetic diversity as judged by isoenzyme and antigenic pattern as well as the sensitivity to anti-malarial drugs[5,6]. To initiate such studies on Indian isolates of *P. falciparum*, the adaptation of isolates from different regions of India, to *in vitro* culture, is a pre-requisite. Three Indian isolates of *P. falciparum* (FAN-5 from Rajasthan[7], MRC from Haryana[8] and FCK-2 from Karnataka[9]) have been adapted to *in vitro* culture and used for serological and seroepidemiological studies.

In the present study we have established an isolate (DCK-I) of *P. falciparum* (from Lucknow, UP) in *in*