Grafting of Polyacrylamide on to Guar Gum using $K_2S_2O_8$ Ascorbic Acid Redox System

U.D.N. BAJPAI, ALKA JAIN, and SANDEEP RAI, *Department of Post Graduate Studies and Research in Chemistry, Rani Durgavati Vishwavidyalaya, Jabalpur 482 001, India*

Synopsis

The grafting of polyacrylamide on to guar gum in aqueous medium initiated by the potassium persulfate/ascorbic acid redox system has been studied gravimetrically at the temperature $35 \pm 0.2°C$ in the presence of atmospheric oxygen and Ag^+ ions. The rate of grafting was found to increase with temperature, concentration of redox components, acrylamide, and guar gum. But at higher concentration of guar gum, the rate of grafting was found to decrease. A mechanism for grafting and suitable rate expression have been suggested.

INTRODUCTION

Guar gum is a nonionic, branched chain polymer. It consists of straight chains of mannose units joined by β-D$(1 \rightarrow 4)$ linkages having α-D galactopyranose units attached to this linear chain by $(1 \rightarrow 6)$ linkages. Guar gum forms viscous, colloidal, dispersion when hydrated in cold water. It is being used as a viscosity builder and water binder in many industries like mining, textile, explosives, paper, petroleum, etc. Although advantageous, this viscosity is difficult to control and that is why it is rarely used in its natural form. Solutions of guar gum are stable for a shorter time.

Modification may be done in many ways, viz. (i) by grafting onto several water soluble vinyl monomers and (ii) by derivatization of its functional groups. It is shown that modified guar gum has better properties and applications than natural guar gum. Literature is available on the derivatization of guar gum but there is insufficient data on modification of guar gum by grafting onto vinyl monomers[1-4]. By graft copolymerization, there is retention of desirable properties of the original polymer, and incorporation of favorable properties.

Several workers[5] have used the easy process of vinyl graft copolymerization through chemical initiation. Grafting of vinyl monomers onto wool, nylon, and fibers through redox initiation has been investigated in detail,[5] but the grafting of water-soluble vinyl monomers onto water-soluble natural polymer is quite rare.

This paper reports the results of grafting of polyacrylamide onto guar gum in aqueous medium using persulfate/ascorbic acid redox system at $35 \pm 0.2°C$ in the presence of Ag^+ ion and atmospheric oxygen.

EXPERIMENTAL

Acrylamide (E. Merck) was recrystallized twice from methanol (G.R.) and dried in vacuum. Ascorbic acid and potassium persulfate (B.D.H. Analar

CCC 0021-8995/90/11-122187-18$04.00

Grade) were used without further purification. Commercial guar gum was purified by dissolving in water and reprecipitating in methanol. All solutions were prepared in doubly distilled water.

Graft Copolymerization

A calculated amount of purified guar gum, acrylamide, ascorbic acid, and silver nitrate were taken in 25 mL water in a 250 mL conical flask and thermostated at temperature (35 $\pm$ 0.2°C). After 30 min a definite quantity of potassium persulfate was added, and this time of addition of persulfate was taken as zero time.

The separation of guar-gum-g-polyacrylamide from polyacrylamide formed in the system was done by the technique described earlier.[6] The method of calculating percentage grafting and grafting efficiency has been described in Bajpai and Rai.[6]
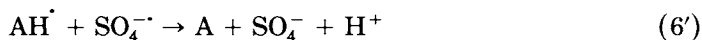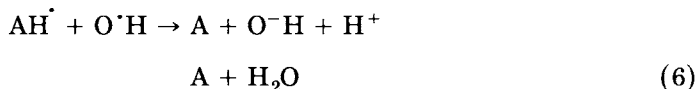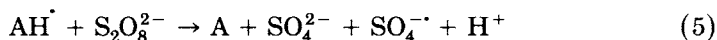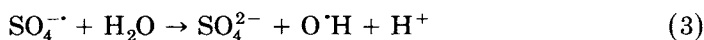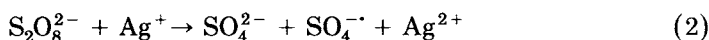
RESULTS AND DISCUSSION

Mechanism

The kinetics of the redox system containing ascorbic acid and peroxydisulfate was studied by Mushran and Mehrotra[7] and a mechanism involving $SO_4^{-\cdot}$ $OH^{\cdot}$, and ascorbate radical intermediates was proposed. This redox system has been exploited for the polymerization of vinyl monomers by several workers.[7,8] Peroxydisulfate ascorbic acid initiated graft copolymerization was found to be catalyzed in the presence of Ag^+. The overall reaction mechanism for the graft copolymerization by this system peroxydisulfate–AA–Ag^+ may be proposed as follows.
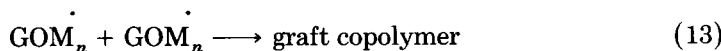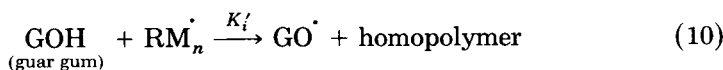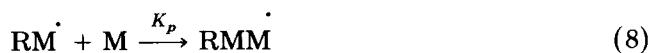
Formation of Free Radicals

The reaction between peroxydisulfate and ascorbic acid involves chain mechanism because of the production of sulfate ion radicals which are well known as chain caniers:

$$S_2O_8^{2-} \rightarrow 2SO_4^{-\cdot} \tag{1}$$

$$S_2O_8^{2-} + Ag^+ \rightarrow SO_4^{2-} + SO_4^{-\cdot} + Ag^{2+} \tag{2}$$

$$SO_4^{-\cdot} + H_2O \rightarrow SO_4^{2-} + O^{\cdot}H + H^+ \tag{3}$$

$$O^{\cdot}H + AH^- \rightarrow AH^{\cdot} + OH^- \tag{4}$$

$$AH^{\cdot} + S_2O_8^{2-} \rightarrow A + SO_4^{2-} + SO_4^{-\cdot} + H^+ \tag{5}$$

$$AH^{\cdot} + O^{\cdot}H \rightarrow A + O^-H + H^+$$
$$A + H_2O \tag{6}$$

$$AH^{\cdot} + SO_4^{-\cdot} \rightarrow A + SO_4^- + H^+ \tag{6'}$$

Misra and Gupta[9] reported the formation of a complex between the monomer and peroxydisulfate which later dissociates to liberate initiating primary free radicals, but the existence of such a complex was not verified by the authors. Roskin[10] proposed that the hydroxyl radical formed in the system [eq. 3] also takes part in the initiation but this could not be verified on the basis of end group analysis of homopolymers obtained by the system.

Mechanism

$$R^{\cdot} + M \xrightarrow{K_i} R\dot{M} \tag{7}$$

$$R\dot{M} + M \xrightarrow{K_p} R\dot{M}M \tag{8}$$

$$R\dot{M}_{n-1} + M \xrightarrow{K_p} R\dot{M}_n \tag{9}$$

$$\underset{\text{(guar gum)}}{GOH} + R\dot{M}_n \xrightarrow{K_i'} G\dot{O} + \text{homopolymer} \tag{10}$$

$$G\dot{O} + M \xrightarrow{K_p'} GO\dot{M} \tag{11}$$

$$GO\dot{M} + nM \xrightarrow{K_p'} GO\dot{M}_n \tag{12}$$

$$GO\dot{M}_n + GO\dot{M}_n \longrightarrow \text{graft copolymer} \tag{13}$$
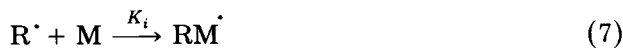
It is apparent from the above reactions that $SO_4^{-\cdot}$ or $AH^{\cdot}$ may initiate graft copolymerization by H abstraction from guar-gum backbone. However, we have proposed the generation of guar-gum macroradical (GO˙) by eq. (10) since initiation of vinyl polymerization is a faster reaction than H abstraction by primary radicals.

RATE EXPRESSION

Rate of Grafting

$$R_g = K_p(\text{GOM}^{\cdot})(\text{M}) \tag{14}$$

On applying steady state conditions the rate expression may be derived as

$$R_g = K[\text{M}][S_2O_8^{2-}]^{1/2}[\text{AA}]^{1/2}[\text{Ag}^+]^{1/2}[\text{GOH}]^x \tag{15}$$

[AA] stands for ascorbic acid which is equivalent to $[AH^-]$. Here x may vary depending upon its concentration. This theoretical expression thus proves the results of our experiment.

Effect of Molecular Oxygen

Molecular oxygen plays an important role in this system. Generally in free radical polymerization oxygen plays an inhibiting role, but in the present system the molecular oxygen acts favorably, which is visible by rapid rate and

negligible induction period. It behaves as a cocatalyst in the present studied system. Cocatalytic activity[10] of molecular oxygen may be due to its reaction with ascorbic acid, producing dehydroascorbic acid which accelerates the formation of free radicals as per the following scheme:
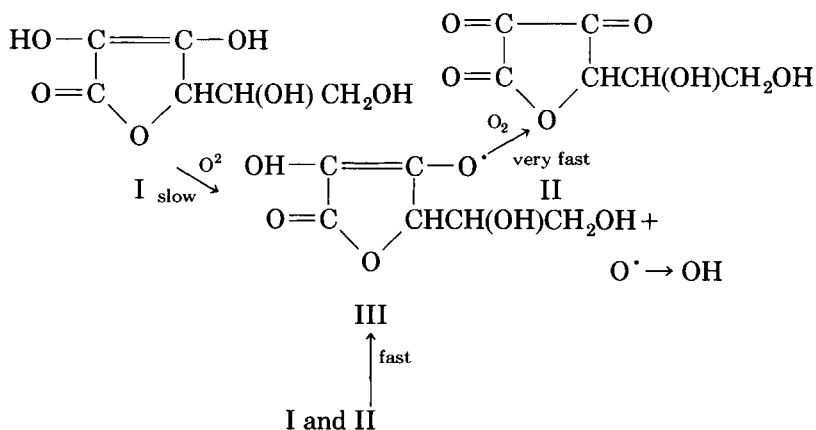
The role of molecular oxygen in minimizing the induction period in such system is of great importance industrially.

Ascorbic Acid Effect

The effect of ascorbic acid is studied in the range $(11 \times 10^{-3}$ to 36×10^{-3} M/L) at fixed concentration of acrylamide $(10 \times 10^{-2}$ M/L), potassium persulfate $(1 \times 10^{-3}$ M/L), and $AgNO_3$ $(8 \times 10^{-5}$ M/L).

It is observed that both percentage grafting [Fig. 1(a)] and percent efficiency [Fig. 1(b)] increases with ascorbic acid concentration within certain range. In the presence of ascorbic acid, $AH^{\cdot}$ radical and $SO_4^{-\cdot}$ radicals generated in the system by the reaction [eqs. (1)–(4)] increase in concentration of these radicals with increase in concentration of ascorbic acid may be responsible for the higher rate of grafting. At higher $(47 \times 10^{-3}$ M/L) ascorbic acid concentration, decrease in percent and efficiency of grafting is observed, which may be due to increased formation of sulfate ions [eq. (5)].

The order of reaction with respect to ascorbic acid as determined from the double log plot between rate of grafting (% grafting/time) and ascorbic acid concentration in M/L [Fig. 1(c)] was found to be 0.55.

AgNO_3 Effect

The $K_2S_2O_8$ ascorbic acid system works well for grafting in the presence of molecular oxygen. Addition of Ag in the concentration of 4.0×10^{-5} mol/L brought about significant increase. In the present experimental conditions, persulfate/Ag^+ or ascorbic acid/Ag^+ does not initiate polymerization to bring about effective grafting.

Potassium Persulfate Effect

The change in percentage and efficiency of grafting at varying concentration of the persulfate $(4.0–10 \times 10^{-3}$ M/L) at fixed concentration of acrylamide
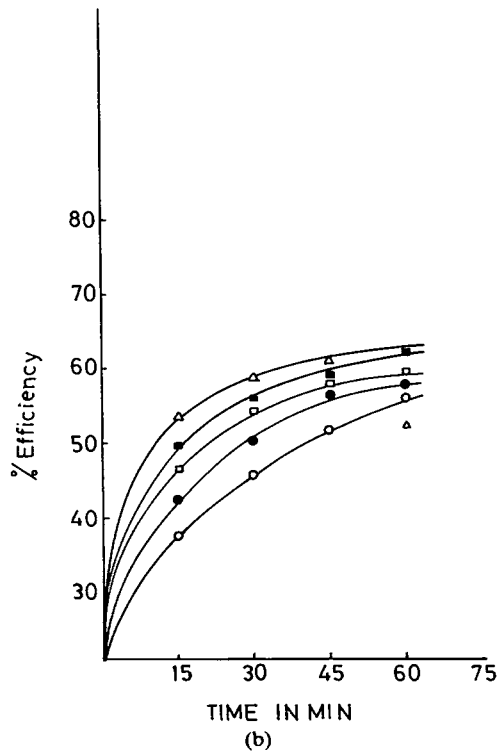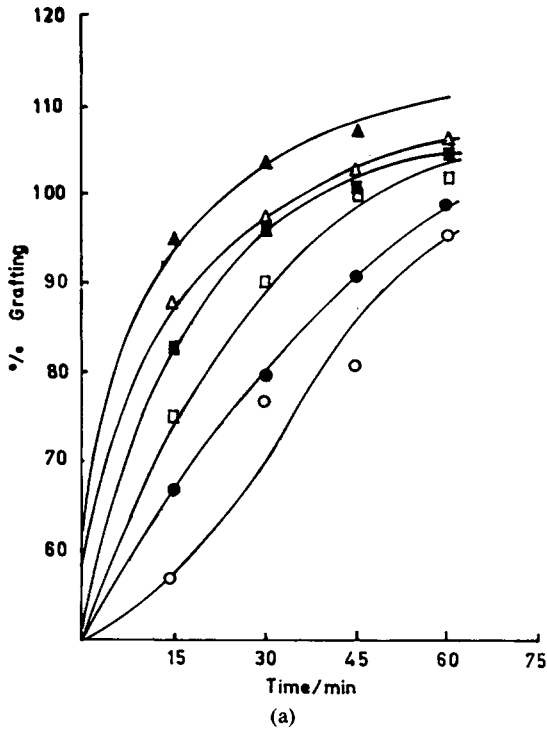
Fig. 1(a) and (b). Time vs. % grafting and % efficiency curve for the grafting of acrylamide with varying concentration of ascorbic acid at fixed concentration of 8×10^{-5} M/L, (AgNO$_3$), (acrylamide), 10×10^{-2} M/L, (K$_2$S$_2$O$_8$), 1×10^{-3} M/L, (guar gum), 0.1 g, temperature 35°C; (●) 11×10^{-3} M/L; (□) 15×10^{-3} M/L; (■) 10×10^{-3} M/L; (△) 22×10^{-3} M/L; (▲) $36 \times 10 \times 10^{-3}$ M/L; (○) 47×10^3 M/L.

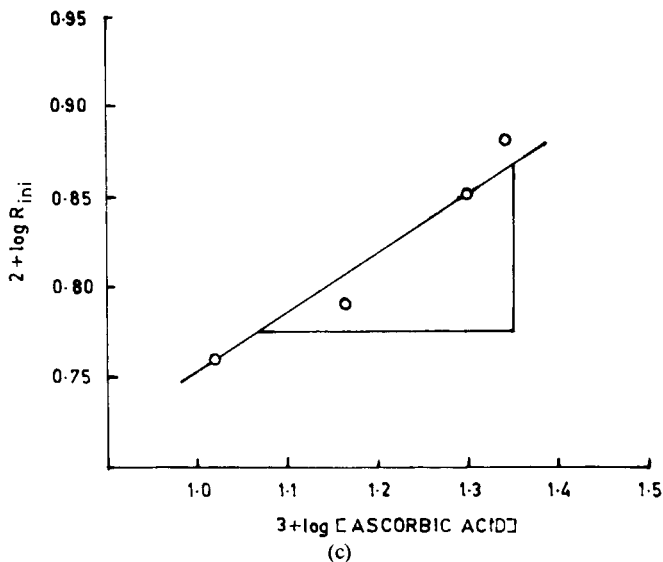Fig. 1(c).   Double logarithmic plot of the initial rate of grafting (R_{ini}% grafting per minute) vs. initial concentration of ascorbic acid.

$(10 \times 10^{-2}$ M/L), ascorbic acid $(22 \times 10^{-3}$ M/L), guar-gum (0.1 gm), $AgNO_3$ $(8 \times 10^{-5}$ M/L) is shown in Figures 2(a) and 2(b).

The increase in percent and efficiency of grafting with persulfate concentration is due to generation of more primary radicals [eqs. (2)–(5)]; the number of propagating radicals thereby increase the number of grafted sites on the backbone of guar gum. The observed order with respect to persulfate concentration is 0.3 from double log plot [Fig. 2(c)] while the predicted order according to proposed mechanism is 0.5. Such a difference has been found in some other cases also and may be attributed to primary radical termination.[5]

Monomer Effect

The initial rate of grafting was found to increase with an increase in initial concentration of monomer in the range $8–16 \times 10^{-2}$ M/L, keeping other ingredients constant [Fig. 3(a)].

The increase in rate of grafting with increase in acrylamide concentration may be due to the formation of more $M_n^{.}$ radicals, which in turn may generate more grafting sites on guar gum by abstraction of H atom. The order of reaction with respect to acrylamide concentration as obtained from double log plot [Fig. 3(b)] was found to be 1.0.

Guar Gum Effect

Effect of guar gum on grafting was studied in the range (0.05–0.2 g) at fixed concentration of acrylamide $(10 \times 10^{-2}$ M/L), ascorbic acid $(22 \times 10^{-3}$ M/L), $AgNO_3$ $(8 \times 10^{-5}$ M/L) and $K_2S_2O_8$ $(1 \times 10^{-3}$ M/L) and is shown in Figure 4.

It has been found that both percent and efficiency of grafting increase with guar gum in a certain range (0.05–0.14 g) (Tables IA and IB). Increase in percent grafting and efficiency at a higher concentration may be due to
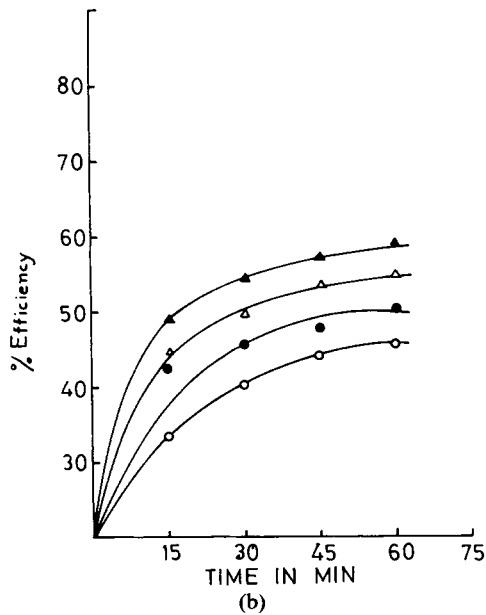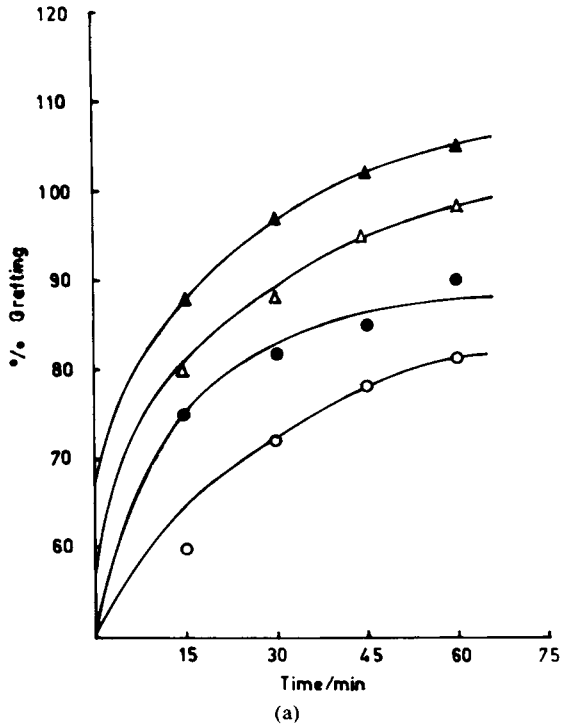
Fig. 2(a) and (b). Time vs. % grafting and % efficiency curve for the grafting of acrylamide with varying concentration of potassium persulphate at fixed concentration of ($AgNO_3$), 8×10^{-5} M/L, (acrylamide), 10×10^{-2} M/L, (ascorbic acid), 22×10^{-3} M/L, (guar gum) 0.1 g, temperature 35°C; (○) 4×10^{-3} M/L; (●) 6×10^{-3} M/L; (△) 8×10^{-3} M/L; (▲) 10×10^{-3} M/L.
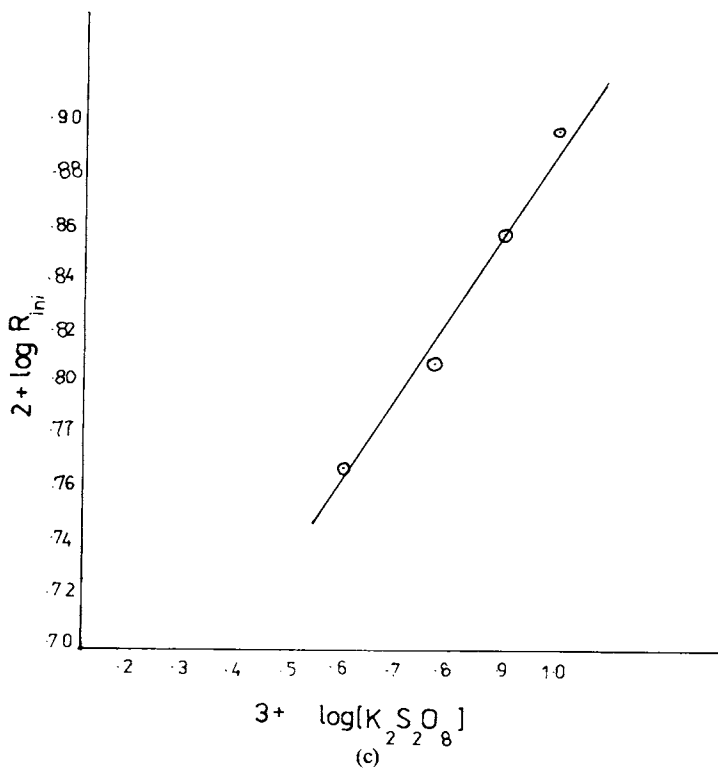
Fig. 2(c). Double logarithmic plot of the initial rate of grafting (R_{ini}% grafting per minute) vs. the initial concentration of potassium persulphate.

availability of more guar gum chains for grafting. It is also possible that at higher concentrations some of the guar gum molecules react with primary radicals to generate backbone macroradicals such as

$$GOH + R^{\cdot} \rightarrow GO^{\cdot} + RH \qquad (16)$$

At higher quantity of guar gum (above 0.14 g) a decrease in grafting is observed which may be due to the increase in viscosity of the medium causing hindrance in normal graft copolymerization.

Temperature Effect

The rate of grafting and efficiency have been found to increase with increase in temperature from 25 to 50°C [Fig. 5(a)] at constant concentrations of other ingredients.

The increase in grafting percentage and efficiency at higher temperature may be due to:

(i) Increased number of collisions between the monomer and guar gum molecules that results due to a decrease in the viscosity of the medium.

(ii) Formation and propagation of active sites on backbone polymer due to higher rate of generation of primary radicals.

(iii) Enhancement in the activity of monomer.
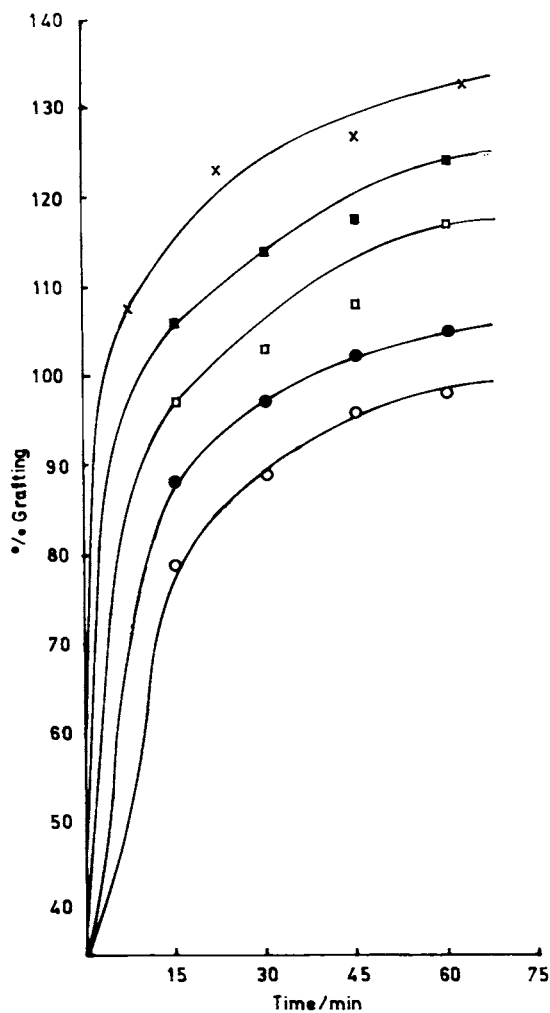
(a)

Fig. 3(a). Time vs. % grafting curve for the grafting of acrylamide with varying concentration of monomer at fixed concentration of ($AgNO_3$) 8×10^{-5} M/L, (ascorbic acid), 22×10^{-3} M/L, ($K_2S_2O_8$), 1×10^{-3} M/L, (guar gum), 0.1 g, temperature 35°C; (○) 8×10^{-2} M/L; (●) 10×10^{-2} M/L; (□) 12×10^{-2} M/L; (■) 14×10^{-2} M/L; (×) 16×10^{-2} M/L.

The overall activation energy as calculated from the slope of the Arrhenius plot [Fig. 5(b)] is 5.98 kcal/mol within the temperature range 25–50°C.

Effect of Addition of Organic Solvents

The effect of organic solvents such as MeOH, EtOH, BuOH, DMF, and dioxane, on grafting, has been studied by addition of 5% v/v of the solvent to the reaction medium. The initial rate of grafting was found to decrease in presence of MeOH, EtOH, BuOH, dioxane, and DMSO, as shown in (Fig. 6), but the limiting rate and percent grafting was found to enhance in case of alcohols. The initial decrease may be due to the fact that addition of these organic solvents reduces the area of hydration layer and thus offers the
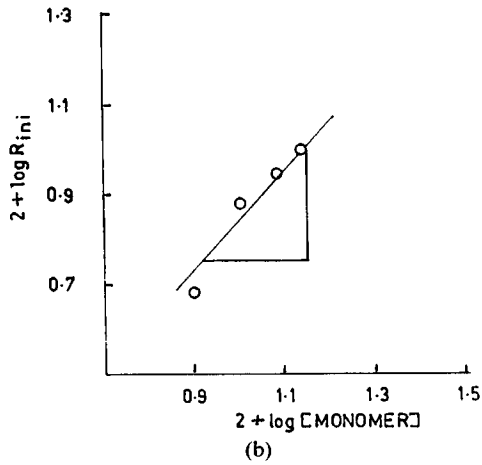
Fig. 3(b). Double logarithmic plot of the initial rate of grafting ($R_{\text{ini}}\%$ grafting/per min) vs. the initial concentration monomer.
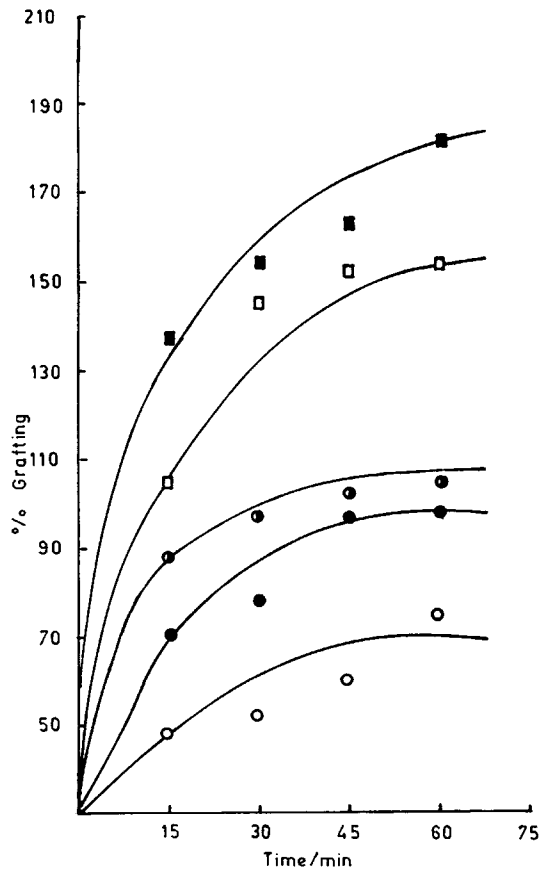

Fig. 4. Time vs. % grafting curve for the grafting of acrylamide with varying concentration of guar gum at fixed concentration of $(AgNO_3)$ 8×10^{-5} M/L, $(K_2S_2O_8)$, 1×10^{-3} M/L, (ascorbic acid), 22×10^{-3} M/L, (acrylamide) 10×10^{-2} M/L, temperature 35°C; (○) 0.05 g; (●) 0.07 g; (◐) 0.1 g; (□) 0.12 g; (■) 0.14 g.

TABLE IA
Effect of Guar-Gum Concentration on Percentage Grafting

Weight of guar gum (g)	Grafting (%)			
	15 min	30 min	45 min	60 min
0.05	48	52	60	75
0.07	70	78	97	99
0.10	88	97	102	105
0.12	105	145	152	155
0.14	138	155	163	182

TABLE IB
Effect of Guar-Gum Concentration on Percentage Efficiency

Weight of guar gum (g)	Grafting efficiency (%)			
	15 min	30 min	45 min	60 min
0.05	27.04	29.29	33.80	42.2
0.07	39.43	43.94	54.64	55.77
0.10	45.57	54.64	57.46	59.15
0.12	59.15	81.69	85.63	87.32
0.14	77.74	87.32	91.83	102.5

macroradical end for premature termination. In the later course of reaction, the increase in grafting rate may be due to the oxidation of alcohols producing more sulfate ion radicals ($SO_4^{-\cdot}$).

In case of DMF, the dielectric constant of the reaction medium is lowered, which favors the formation of sulfate radical ion ($SO_4^{-\cdot}$) by (2), and this in turn increases rate and percentage of grafting. In reaction (2) of the proposed mechanism, as two oppositely charged ions are involved, the rate of this reaction will increase with decrease in dielectric constant of the medium.[11]

Effect of Salts

The addition of small amounts of inorganic salts viz. LiCl, KCl and NaCl have been found to accelerate grafting (Fig. 7). This may be explained as:

Addition of cations to the reaction medium bring about two opposing effects in aqueous medium.

(i) The hydrated cations interact with $SO_4^{-\cdot}$ ion and these produce more $OH^{\cdot}$ radicals [eq. (3)] which results in an increase in rate of grafting.

(ii) Due to hydration of these cations, the availability of water molecules in the bulk of the solution decreases and the equilibrium of reaction $AH_2 = AH^- + H^+$ shifts towards the right, thereby resulting in an increase in the rate of generation of $AH^{\cdot}$ radicals [eq. (4)] and an increase in rate of grafting is observed.

Since the dielectric constant of reaction medium is lowered,[11] it results in a greater electrostatic attraction between the hydrated cation and the SO_4^- ion also therefore (i) is preferred, which will bring an increase in grafting rate since Li^+ ion is the largest hydrated ion; reaction (2) will be more effective
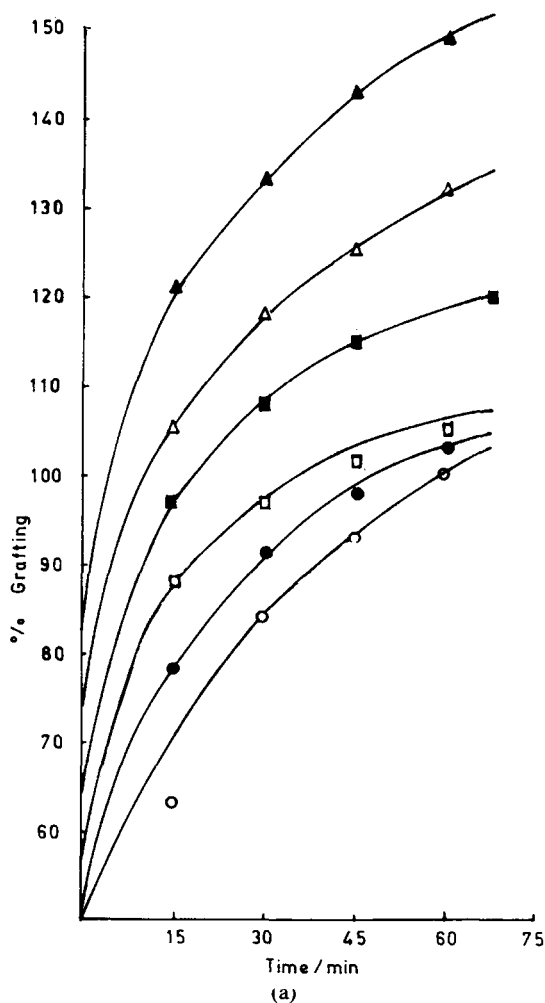
Fig. 5(a). Time vs. % grafting curve for the grafting of acrylamide with varying temperature of the reaction, keeping other ingredients constant: (○) 25°C; (●) 32°C; (□) 35°C; (■) 40°C; (△) 45°C; (▲) 50°C.

with Li^+, in comparison to Na^+ and K^+ ions, resulting in an increase in rate of grafting in the order

$$Li^+ < Na^+ < K^+$$

On the other hand, the addition of anions, such as Cl^-, and Br^-, reduces the rate of grafting whereas that of I^- ions increases the rate. The addition of Cl^- and Br^- increases the ionic strength of the medium, which may result in premature termination of the grafting radical chain. The increase in grafting rate by addition of I^- ions is due to their oxidation by presulfate ions, which produces sulfate radicals $(SO_4^{-\cdot})$ in the system and therefore increases the rate.

Effect of Surface Active Agents

The influence of surfactants on the rate of graft copolymerization is shown in Figure 8. It is clear from this figure that both cationic (CTAB) and anionic
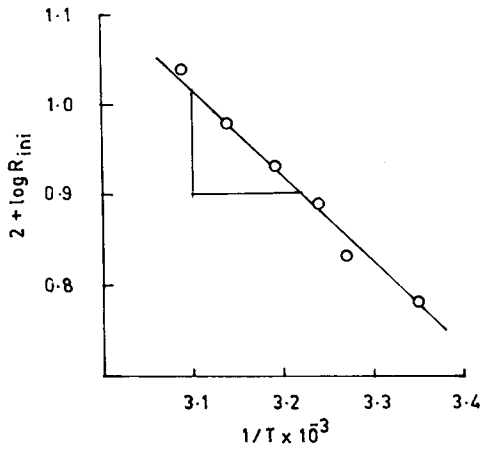
Fig. 5(b). Arrhenius plot of the initial rate of grafting (R_{ini}) vs. reciprocal of absolute temperature ($1/T$) of grafting energy of activation E_a = 5.98 kcal/mol.
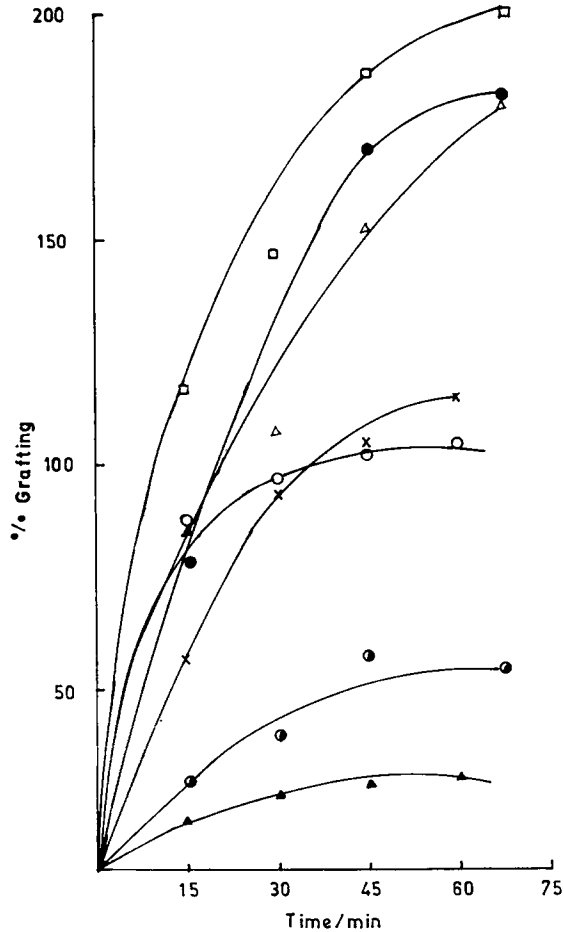

Fig. 6. Time vs. % grafting curve for the grafting of acrylamide showing the effect of addition of solvent (by volume) at fixed concentration of (AgNO$_3$), 8 × 10^{-5} M/L, (acrylamide) 10 × 10^{-2} M/L, (ascorbic acid), 22 × 10^{-3} M/L, (K$_2$S$_2$O$_8$), 1 × 10^{-3} M/L, temperature 35°C; (▲) dioxane; (◐) DMSO; (○) control; (×) EtoH; (△) butanol; (●) MeOH; (□) DMF.
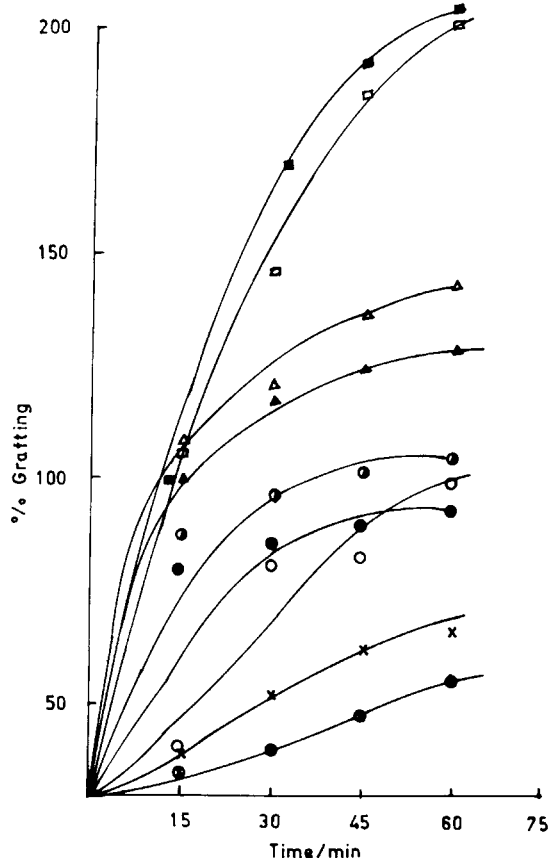
Fig. 7. Time vs. % grafting curve for the grafting of acrylamide showing the effect of added neutral salts and complexing agents (in equal amount) at fixed concentration of (acrylamide), 10 $\times$ 10^{-2} M/L, (AgNO$_3$), 8 $\times$ 10^{-5} M/L, (ascorbic acid) 22 $\times$ 10^{-3} M/L, (K$_2$S$_2$O$_8$), 1 $\times$ 10^{-3} M/L, temperature 35°C; ($\oplus$) NaF; (x) EDTA; ($\bullet$) KCl; ($\circ$) KBr; ($\mathbf{O}$) control; ($\blacktriangle$) Li$_2$SO$_4$; ($\triangle$) Na$_2$SO$_4$; ($\square$) K$_2$SO$_4$; ($\blacksquare$) KI.

(sodium oleate) surfactants decrease the rate of grafting and limiting conversion, at values both below and above their critical miceller concentration (CMC).

The depression caused by the surfactant CTAB may be explained by assuming a specific ion pair binding of ascorbate anion (AH$^-$) with the large cation R$_4$N$^+$, thus reducing the AH$^-$ concentration taking part in the production of primary radicals [eq. (4)].

The observed decrease in the rate of polymerization and limiting conversion on the addition of anionic surfactants (sodium oleate) may be explained by the fact that Ag$^+$ ions get absorbed on the surface of anionic micelles, which results in a lower rate of generation of primary radicals [eq. (2)], thus causing a decrease in the rate of polymerization.

Effect of Complexing Agents

The complexing agents like EDTA and sodium fluoride have been found to decrease the rate and percentage of grafting (Fig. 8). The depression caused by EDTA may be explained by one of the following facts.
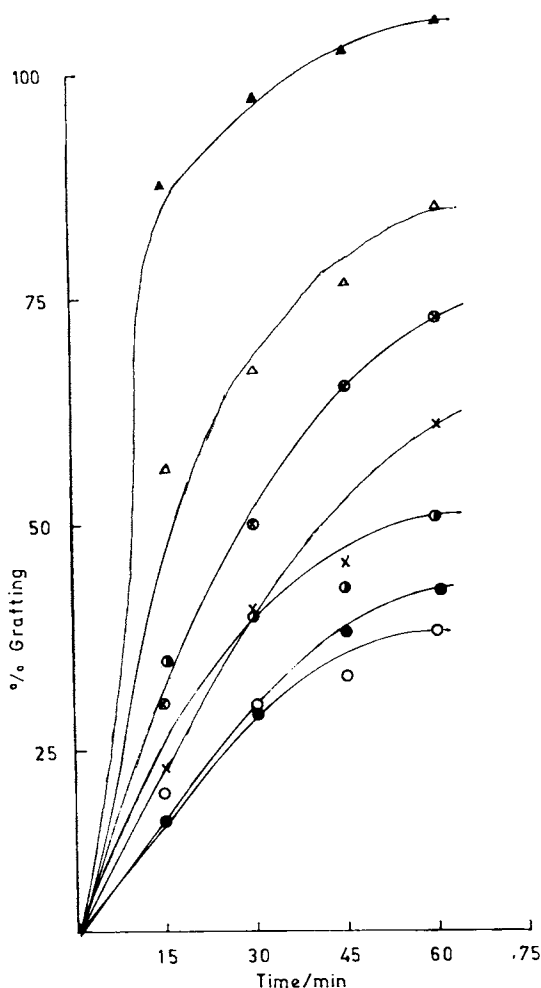
Fig. 8. Time vs. % grafting curve for the grafting of acrylamide showing the effect of added surfactants below and above their critical miceller concentration (CMC) at fixed concentration of other parameters: (○) CTAB (below CMC); (●) sodium oleate (below CMC); (◑) CTAB (CMC); (×) sodium oleate (CMC); (⊕) sodium oleate (above CMC); (△) CTAB (above CMC); (▲) control.

(1) Silver ions (Ag^+) which are known to form a colorless adduct with the ion pair of electron on oxygen atom may form the same with oxygen atom of carboxylic group in EDTA. The Ag^+ ions are thereby prevented from participating in radical generation step [eq. (5)], consequently decreasing the rate of grafting.

(2) The oxidation of EDTA by the oxidant may produce free radicals ($Z^{\cdot}$), which may at once react with the $SO_4^{-\cdot}$ radical to give a nonradical ion as shown below:

$$Z^{\cdot} + SO_4^{\cdot -} \rightarrow Z : SO_4^{-} \tag{17}$$

Thus a decrease in $SO_4^{-\cdot}$ radical concentration brings about a depression in the rate.

The possibility of formation of a stable chelate between Ag^+ ion and EDTA cannot be ruled out, which may also bring about a decrease in the rate of grafting. The addition of NaF, a known complexing agent, lowers the rate of grafting, due to formation of a complex of the type AgF_2^- between polarized Ag^+ and F^- ions. The participation of Ag^+ ion in the radical generation step [eq. (2)] is restricted and a depression in the initial rate and limiting conversion is observed.

Determination of Cohesive Energy Density of Grafted Guar Gum by Swelling Measurements

The cohesive energy density (c.e.d.) of a polymer guar gum is the closest approximation of its solubility prediction provided that some specific interaction between the grafted guar gum solvent are not present. The value of c.e.d. also depends on the chemical structure and different constituent groups present in the guar gum.[12] Experimental determination of c.e.d. values for a number of polymers has been done by measuring the swelling coefficients in a series of liquids. Some other method of c.e.d. determination involves the use of
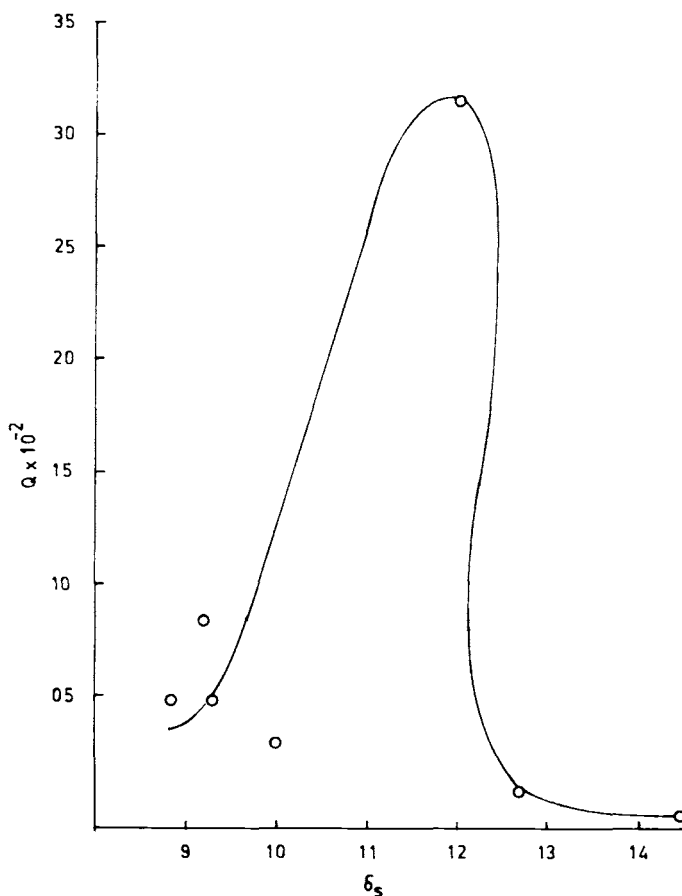

Fig. 9.   A plot between swelling coefficient Q and δ_s.

viscosity measurements. All measurements were made at room temperature, i.e., 25°C.

The swelling coefficient Q was calculated using the following relationship:

$$Q = \left(\frac{m - m_0}{m_0} \right) \times \frac{1}{d} \tag{18}$$

where m = weight of swollen grafted guar gum, m_0 = weight of unswollen grafted guar gum, and d = density of the liquid initially.

According to the treatment of Hildebrand and Scot[13] and Scatchard,[14] the heat of mixing per unit volume only when depression forces are involved is

$$\Delta H = \phi_s \phi_p \left(\delta_s - \delta_p \right)^2 \tag{19}$$

where ϕ_s and ϕ_p are the volume fractions of solvent and polymer and δ_s and δ_p are solubility parameters given by

$$\delta = \left(\Delta E / V \right)^{1/2} \tag{20}$$

$\Delta E / V$, the energy of vaporization per unit volume, is also termed as cohesive energy density. From Eq. (19), Gee et al.[15] concluded that the maximum swelling of polymer will occur when $\delta_p \simeq \delta_s$. Hence a plot between the swelling coefficient Q and δ_s values of the solvent give a Guassian curve where maxima
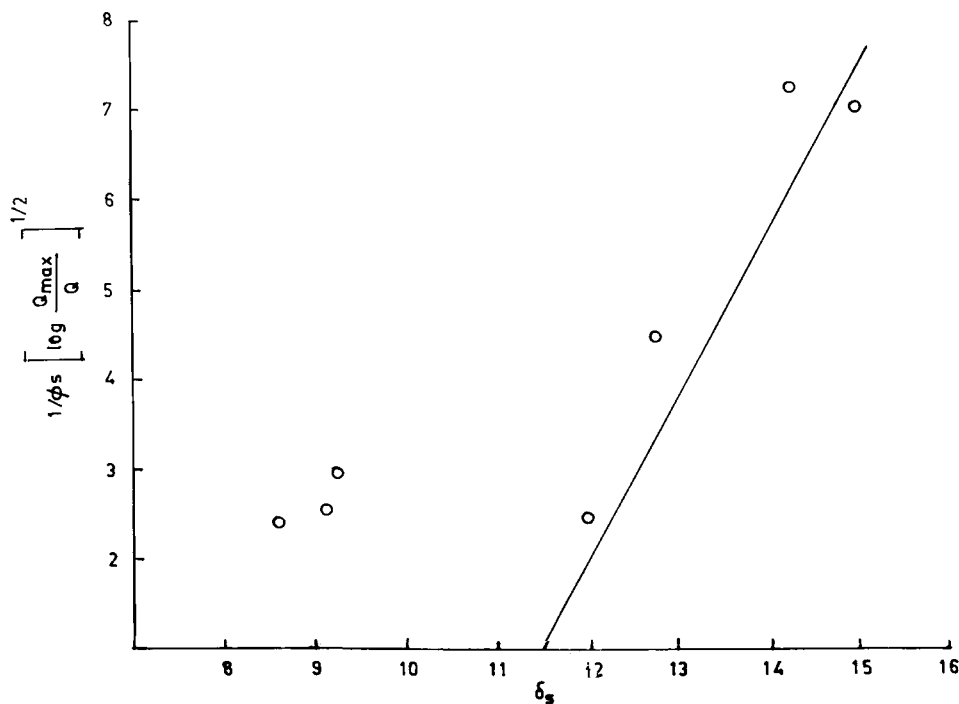

Fig. 10. A plot between and $1/\phi_s [\ln(Q_{max}/Q)]$ and δ_s.

corresponds to s_p as shown in Fig. 9. It was also shown that

$$Q = Q_{max} \bar{e} (\delta_s - \delta_p)^2 \phi_s \qquad (21)$$

A plot of $(1/\phi s) [\log(Q_{max}/Q)]^{1/2}$ versus δ_s is a straight line, the intercept on X-axis gives δ_p (Fig. 10). The values of Q have been plotted against δ_s from the plot where Q_{max} was obtained. The values of δ_p obtained in both cases are approximately the same.

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