ELECTROCHEMICAL SYNTHESIS OF POLYACRYLAMIDE IN TWO PHASE MEDIA

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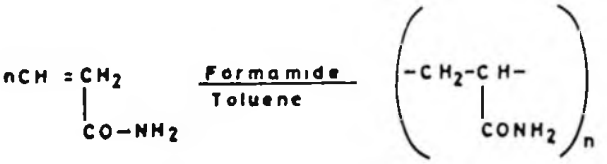
Acrylamide has been polymerised electro chemically in two phase media giving polymers of molecular weight 10^6 as in poly methylmethacrylate. Ferric sulphate has been used as an electrolyte to catalyse the polymerization process. Polyacrylamide was obtained in good yield with highest R_p of 0.962% per hour and the highest polymerization efficiency of 31.29 moles per faraday. A free radical mechanism of polymerization has been postulated.

Polyacrylamide, a white, water soluble, high polymer, is used as a thickening agent and flocculant. So far the polymerization of acrylamide [1] has been reported in a single homogeneous phase consisting of solvent, electrolyte and monomer. The method of electropolymerization in two phase media [2,3] is extended to this polymerization also.

The two phases were kept in intimate contact with each other by stirring to facilitate the transfer of free radicals formed in polar phase to the non polar phase.

Formamide is used as polar phase because of its high dielectric constant (109.5 at 296.15° K). The non polar phase being the solution of acrylamide in Toluene/Xylene. Efficiency of several other electrolytes including acetates of zinc and potassium have been examined in this medium.

The overall process can be represented as



Acrylamide (AA) Polyacrylamide (PAA)

EXPERIMENTAL

Materials

Acrylamide (Fluka) was recrystallised from ethanol and dried in vacuum. Formamide (Aldrich) was purified by procedure described by Nayak et al [4]. Toluene, Xylene (Ranbaxy) were used without further purification.

Anhydrous ferric and ferrous sulphate, anhydrous ferric chloride, zinc acetate, sodium acetate, (all BDH reagents) were used without any further purification.

The cell assembly and the electrolysis are as described in the previous paper [3].

During electrolysis metallic depositions were found on cathode but to reduce it to minimum, the polarity of electrodes were changed after every hour. In order to determine the yield of polymers at a certain interval of time, the electrolysis was terminated, the whole of non polar phase was precipitated by excess of acidified methanol and resulting white insoluble polymers were dried in an oven at 100° C.

The average molecular weight of polymers was determined in water by viscometry [5,6], using the relation.

$$\eta = K M_v^a$$

RESULTS

Polymers obtained in the absence of electrolytes have very low molecular weight and are produced to a very small extent over a period of 3-4 hours.

Effect of Supporting Electrolytes and Solvent

The result of electropolymerization of acrylamide in xylene and toluene is summarised in Table 1. The polymerization is observed, to be dependant upon the nature of cation used as supporting electrolytes. It shows that ferric salts are the most effective in producing polymers of both higher molecular weights and higher yield.

TABLE 1

ELECTROPOLYMERIZATION OF ACRYLAMIDE (AA) AT 30 ± 1°C CONTAINING DIFFERENT SALTS AT A FIXED CURRENT OF 15 mA IN TOLUENE/XYLENE. ELECTROLYSIS TIME = 4 HOURS [AA] = 1.5 MOL/LITRE

Volume of polar and non polar solvent = 50 ml each

Electrolytes	Yield in gms. of polymer in		% Conversion	Toluene Rp %hr.	moles of monomer polymerized/faraday
	Toluene	Xylene			
Ferric sulphate	0.1493	0.1423	2.804	0.701	18.80
Ferrous sulphate	0.1455	0.1368	2.732	0.683	18.31
Ferric chloride	0.1460	0.1368	2.742	0.685	18.38
Zinc chloride	0.1360	0.1356	2.554	0.638	17.12
Zinc acetate	0.1405	0.1374	2.638	0.660	17.68
Potassium acetate	0.1330	0.1320	2.498	0.624	16.74

The effect of ferric sulphate concentration on the rate of polymerization at two different current strengths 5 mA and 15 mA is shown in Fig. 1. It shows that in both the cases the rate of polymerization increases with increasing electrolyte concentration and attains a maxima before reaching a constant value at higher concentrations.

Effect of Monomer Concentration

Polyacrylamide obtained with different initial concentration of acrylamide (AA) at a fixed current of 15 mA for $Fe_2(SO_4)_3$, $ZnCl_2$ and $FeSO_4$ is shown in Table 2.

Effect of Current

At three different current (5 mA, 15 mA and 20 mA) the percentage of conversion with respect to time of electrolysis is depicted in Fig. 2. The figure explains that after lapse of some time (Induction period) the percentage of conversion varies linearly with time.

The percentage of conversion as a function of charge passed shows that the percentage of conversion increases with increase in quantity of charge till it reaches a limiting value (Fig.3)

DISCUSSION

The biphasic systems are more suitable for polymerization than the monophasic ones. The presence of air or hydroquinone inhibits the polymerization. This suggests a radical mechanism is operating.

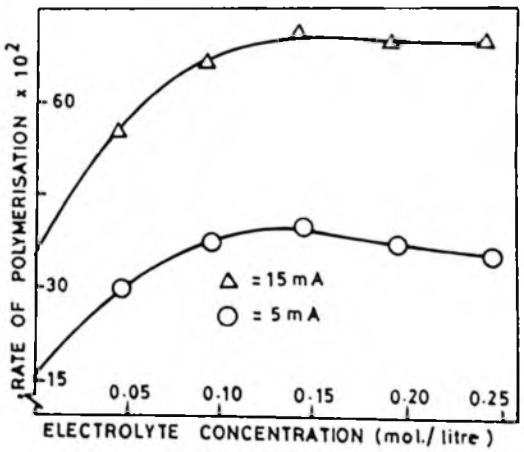


Fig. 1 Rate of polymerization – concentration of ($Fe_2(SO_4)_3$) at 30 ± 1°C [Acrylamide] = 1.5 mol/litre, electrolysis time = 4 hrs. Volume of polar and non polar solvent used = 50 ml each.

Radical formation may take place as per the following mechanism [7].

$$2HCONH_2 \rightleftharpoons HCONH_3^+ + HCONH^-$$

$$HCONH_3^+ + e^- \text{ (cathode)} \longrightarrow HCONH_2 + \dot{H}$$

$$M + \dot{H} \longrightarrow M \text{ (Monomer radical)}$$

TABLE 2

YIELD OF PAA FORMED AT DIFFERENT MONOMER CONCENTRATION IN TOLUENE CONTAINING DIFFERENT ELECTROLYTES AT 30 ± 1° C; CURRENT = 15 mA; ELECTROLYSIS TIME = 4 hrs.

Volume of polar and non polar solvent used = 50 ml. each.

$[Fe_2(SO_4)_3]$ = 0.15 mol/litre		$[ZnCl_2]$ = 0.5 mol/litre		$[FeSO_4]$ = 0.5 mol/litre	
Monomer mol/litre	PAA yield in gms.	Monomer mol/litre	PAA yield in gms.	Monomer mol/litre	PAA yield in gms.
0.50	0.0390	0.50	0.0272	0.50	0.0354
1.00	0.0948	1.00	0.0826	1.00	0.0902
1.50	0.01493	1.50	0.1360	1.50	0.1455
2.00	0.1979	2.00	0.1856	2.00	0.1966
2.50	0.2488	2.50	0.2352	2.50	0.2423

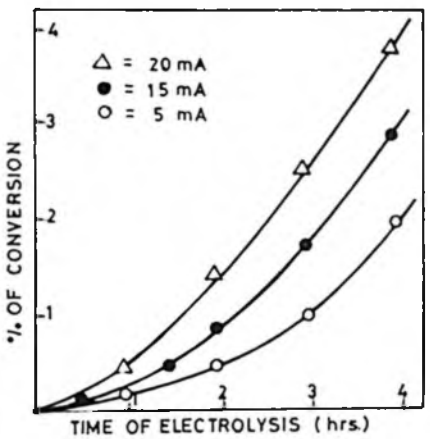


Fig.2 Percentage of conversion for electropolymerisation of acrylamide as a function of time in Toluene at 30 ± 1°C [Acrylamide]=1.5 mol/litre. $[Fe_2(SO_4)_3]$ = 0.15 mol/litre; Volume of polar and non polar solvent used = 50 ml. each.

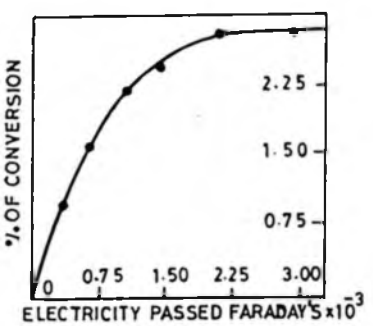


Fig. 3 Percentage of conversion as a function of charge passed at 30 ± 1°C in Toluene [Acrylamide]=1.5 mol/litre, $[Fe_2(SO_4)_3]$ = 0.15 mol/litre, electrolysis time = 4 hrs. Volume of polar and non polar solvent used = 50 ml. each

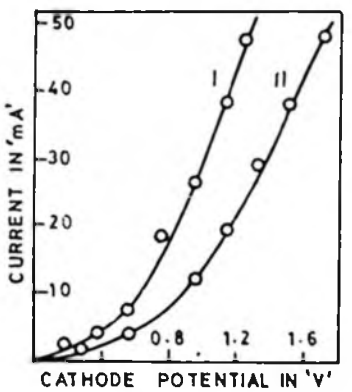


Fig. 4 Plot of current vs. cathodic potential (relative to SCE) for electrolysis $Fe_2(SO_4)_3$ = 0.15 mol/litre Temp. 30 ± 1°C I, without AA; II with 1.50 mol/litre of AA.

The monomer radical thus formed diffuses to the non polar phase to initiate the polymerization.

Polarization curve of solution containing $Fe_2(SO_4)_3$ in formamide at 30 ± 1°C (Fig.4) shows that the cathode potential of $Fe_2(SO_4)_3$ is less negative than that of AA which justifies the radical mechanism.

The role of Fe^{+3} is to prevent the radicals from any recombinations before diffusing into non polar phase by a phenomenon similar to radical stabilization [8].

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