Emulsion Polymerization of Vinyl acetate Using Developed Redox Initiation Systems

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Abstract: The kinetics of emulsion Polymerization of vinyl acetate in presence of polyvinyl alcohol (PVA) as non ionic surfactants using potassium persulphate in coupling with acetone sodium bisulphite (AcSBS) adduct as aliphatic reducing agent and benzaldehyde sodium bisulphite (BSBS)adduct as aromatic reducing one was studied. The results show that the rate of polymerization (Rp) was found to be dependent on the initiator concentration to the powers 1.08 and 0.57 in presence of potassium persulphate/ acetone sodium bisulphite (KPS/AcSBS) and potassium persulphate/ benzaldehyde sodium bisulphite (KPS/BSBS) . While it was dependent on emulsifier concentration to the powers 1.0 and 0.7 for KPS/ACSBS and KPS/BSBS. As well as, the monomer was found to be dependent to the power 0.0.36 and 0.39. The activation energies for the emulsion polymerization of VAc using two reducing agent are as follows 2.48 x10 ^{4}, 5.19 x 10 ^{4} J / mol, The morphological studies of some prepared polyvinyl acetate latex particles reveal that decreasing the concentration of non ionic surfactant the volume average diameter decrease ($\overline{D}$ v).

1. Introduction:

Emulsion polymerization is a free radical initiated chain polymerization in which a monomer or a mixture of monomers is polymerized in the presence of an aqueous solution of a surfactant to form a product known as latex. The latter is defined as a colloidal dispersion of polymer particles in an aqueous medium. Three types of processes are commonly used in emulsion polymerization, batch, semi continuous (or semibatch) and continuous. Semi-batch emulsion polymerization processes generate a large number of polymer particles compared with conventional batch processes [1,2]. Semi batch processes produce more particles than batch processes only if monomer droplets are depleted earlier than surfactant micelles.   The chemical composition of the surfactant influences the compatibility with the polymer, if the surfactant is similar to the polymer, it will dissolve and plasticize the polymer [3, 4] the amount of carboxylic groups in the shell of the particles can modify the chemical compatibility with the surfactant [5, 6]. Polyvinyl alcohol PVA has been used industrially as a dispersant in the synthesis of the copolymer emulsions of vinyl acetate (VAc) .There are several reasons to adopt PVA in the commercial co polymer emulsions of VAc [7], the mechanical properties such as tensile strength and creep resistance are enhanced

by PVA in the emulsion films. This is one of the most important points when the emulsion is utilized in the application field of surface coatings. The addition of alcohol [8] to the emulsion polymerization of VAc using ammonium persulphate (APS) and PVA as a protective colloid remarkably affected the particle formation, especially grafting. This is thought to be attributed to competition between hydrogen abstraction from PVA and alcohol with a sulphate radical. The addition of acetone to the system decreased grafting to a great extent resulting in an increase in the particle size together with an increase in the number of polymer molecules in a polymer particle. In the emulsion polymerization [9]of VAc using PVA as a protective colloid where a small amount of VAc was employed , it is found that in the presence of large amounts of PVA , the number of new particles smaller than 80 nm continued to increase during the polymerization , while there was not much increase in the particle diameter . In contrast, in the absence of PVA, the particles formed at the very early stage continued to grow and the number of particles did not increase so many, the [10] PVA blockiness did not influence greatly the polymerization kinetics in the emulsion polymerization of VAc using different types of PVA where three fractions of PVA are separated in the latex, free in the water phase, physically adsorbed

onto the polymer particles and chemically grafted. The grafted fraction is relatively lower than the physically adsorbed fraction, and the grafted fraction is almost constant with different PVA types. Comparing the latexes [11] obtained in the semi-continuous polymerization of VAc, butyl acrylate BA, Veova 10, and hexafluorobutyl methacrylate using an anionic polymerizable fumaric surfactant a new surfmer and that obtained using sodiumdodecyl sulphate SDS, it is found that the new surfmer behaved much better with respect to the stability of the latexes and the water sensitivity of the films. A nonlinear relationship [12] was observed between the rate of polymerization Rp and the number of particles (N_p) and the final N_p was independent of the degrees of blockiness of PVA on studing the role of grafting in the particle nucleation during the emulsion polymerization of VAc with partially hydrolyzed PVA as a protective colloid and potassium pesulphate KPS as an initiator. On studying [13] the effect of the emulsion polymerization conditions of VAc on the viscosity fluctuation and the gelation behavior of the aqueous PVA solution at 40, 50 and 60ºC, it is found that the viscosity is increased with increasing the molecular weight when other parameters are held constant. On emulsion polymerization[14] of VAc in presence of APS as an initiator , an ethoxylated nonylphenol as a nonionic surfactant and PVA as a protective colloid using semi continuous process , the resultant latex viscosity decreased and the viscosity-average polymer molecular weight increased with increasing the ethoxylation degree of the nonionic surfactant. The increase in the ethoxylation degree did not seriously affect the surface tension of the resultant latex or the surface free energy of the dried PVAc films.

The aim of the present work is to study the effect of different redox initiation systems of the kinetic parameters of the emulsion polymerization of vinyl acetate monomer using poly (oxyethelene - oxypropylene) with molecular weight 80 as non-ionic emulsifiers. These redox initiation systems will be potassium per sulphate with each (Acetone sodium bi-sulfite) as aliphatic reducing agent and (Benzaldehyde sodium bisulfite) as aromatic reducing one.The work will further study the effect of redox initiation system and non-ionic emulsifiers on the morphological characteristic of some prepared polyvinyl acetate latex partials. Finally, the suitable polymerization conditions will be selected to prepare some vinyl acetate - butyl acrylate copolymer lattices with high solid content and high stability to be applied in surface coatings.

2. Experimental

Vinyl acetate (VAc)monomer (stabilized with 14ppm hydroquinone) was provided by Sigma-Aldrich chemical company Ltd. England was redistilled before use and stored at -20ºC. Potassium persulphate (KPS) was recrystallized from water by methanol, and the final crystals were vacuum dried. Polyvinyl alchohol (PVA) 125000 was a product of Vinavil, Italy. Acetone, bezaldehyde and sodium bisulphite are of pure laboratory chemicals. All water used was purified by distillation

Preparation of Sodium Bisulphite Adducts

Benzaldehyde sodium bisulphite (BSBS) and acetone sodium bisulphite (ASBS) adducts were prepared according to the method previously mentioned [15].

Emulsion Polymerization of Vinyl Acetate

The following ingredients were mixed in a 250 ml three necked flask, the order of addition was as follows: water, initiator,   and VAc monomer according to the recipe in Table I. The polymerization reactions were carried out at the required temperature (±2 ºC) in an automatically controlled water bath. All the experiments were run with mechanical stirring at 250 rpm; this speed is in the range where the agitation has no noticeable effect on the rate of polymerization.

Table I: Recipe of emulsion polymerization of vinyl acetate

Ingredient	Function	Amount (Mol/l X10^3)
Vinyl acetate	Monomer	0.00054-.00216
Polyvinyl alchohol	Emulsifier	0.00036- 0.00072
Potassium persulphate/acetone sodium bisulphite or Potassiumpersulphate/benzaldehydesodium bisulphite	Redox initiation system	0.00001-0.00004
Demineralized water	Dispersion medium	Variable

The rate of emulsion polymerization of vinyl acetate, the apparent activation energy, particle diameter and the polydispersity of polymer particle were calculated as mentioned previously [16,17].

3. Results and Discussion
Effect of initiator concentration on the rate of polymerization

Figures (1&2) clear the conversion–time relationships for the emulsion polymerization of VAc monomer (1.06 mol/l) at 50ºC, by using different concentrations of potassium persulphate – acetone sodium bisulphite KPS /AcSBS and potassium persulphate – benzaldehyde sodium bisulphite KPS/BSBS as two different redox initiation systems in presence of PVA (0.54x10^{-3} mol/l) as non-ionic emulsifiers. it is clear that the Rp values as well as the conversion percent increase with increasing the initiator concentration. Moreover, the obtained conversion time curves show a sigmoidal shape similar to that revealed for the classical emulsion polymerization. This is attributed to the increase in the rate of production of the primary free radicals in the reaction medium. From figures (3&4) it is clear that the rate of polymerization Rp was found to be dependent on the initiator concentration to the powers 1.08 and 0.57 in presence of KPS/ASBS and KPS/ BSBS by using PVA as nonionic emulsifier. From these results, it can be concluded that the efficiency of the different redox initiation systems can be arranged as follows : KPS/ASBS > KPS/BSBS and it is clear that in case of redox initiation system KPS/BSBS has lowest power of the reaction, this may be attributed to the high steric hindrance of the formed radicals.
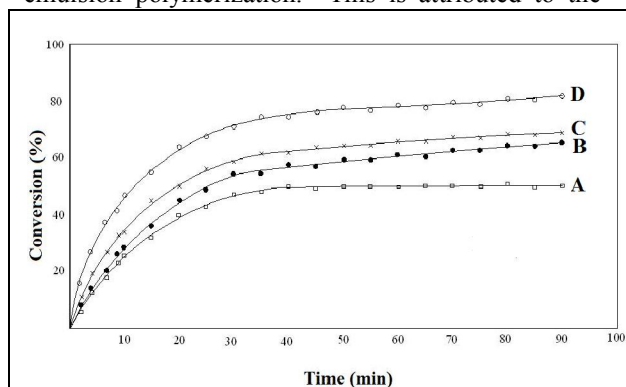

Fig. (1): Conversion-time plot of the emulsion polymerization of VAc in presence of PVA as non ionic emulsifier and different concentrations of KPS/AcSBS as a redox initiation system.

   A-.0.005/0.1 (M)   B-0.1/0.02 (M)
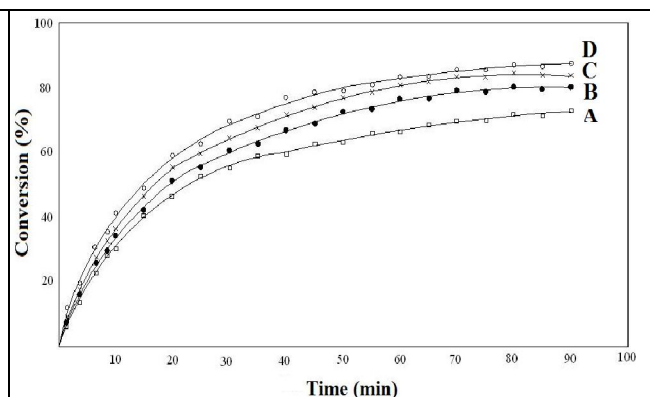   **C-0.015/0.03 (M)   D-0.02/0.4 (M)**

Fig. (2): Conversion-time plot of the emulsion polymerization of VAc in presence of PVA as non ionic emulsifier and different concentrations of KPS/BSBS as a redox initiation system.

   A-.0.005/0.1 (M)   B-0.1/0.02 (M)
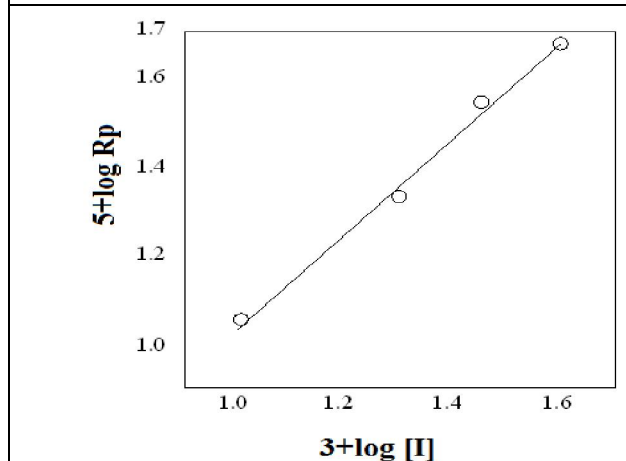   **C-0.015/0.03 (M)   D-0.02/0.4 (M)**

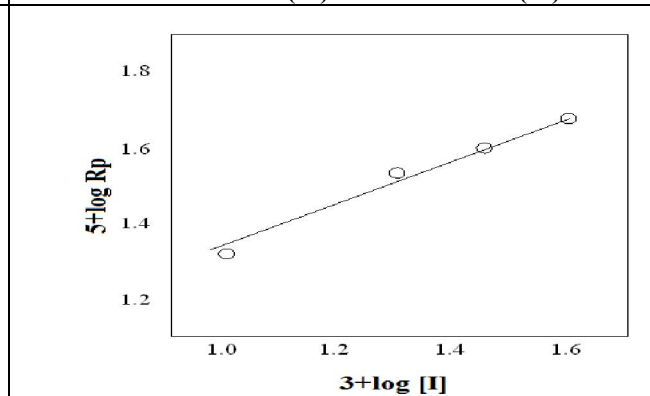Fig.(3): Double logarithmic plots of the Rp of VAc vs. the concentrations of KPS/AcSBS using PVA as an emulsifier.

Fig.(4): Double logarithmic plots of the Rp of VAc vs. the concentrations of KPS/BSBS using PVA as an emulsifier

The redox initiator system consists of KPS with ASBS adduct has a higher Rp and a maximum conversion than the other one, this may be attributed to the low steric hindrance of the formed radicals and this adduct is more suitable for the emulsion polymerization of vinyl acetate as aliphatic adduct act as reducing agent [18]. The rate equation with respect to initiator concentration is as follow:

$$Rp \propto [I]^x$$

Where [I] is the initiator concentration and X was found to be equal 1.00 and 0.57.

Effect of emulsifier concentration on the rate of polymerization

Figures (5&6) clear the conversion–time relationships for emulsion polymerization of VAc at 50^0C using different concentrations of pluronic in presence of developed redox initiation system KPS/AcSBS and KPS/BSBS. The monomer concentration was1.06 mol /l. The conversion curves show a sigmoidal shape of a conventional emulsion polymerization. From Figure (7&8) it is clear that the rate of polymerization (Rp) was found to be dependent on the concentration of PVA to the powers 1.0 and 0.7. The values of powers are deviated from that obtained by micellar model [19] which is expressed as $Rp \propto [E]^{0.6}$. This may be due to the using of aliphatic reducing agent AcBSB which act as well as BSBS aromatic reducing agent. The rate equation with respect to the protective colloid concentration is as follow:

$$Rp \propto [E]^Y$$

Where [E] is emulsifier concentration and Y was found to be equal 1.0 and 0.7.
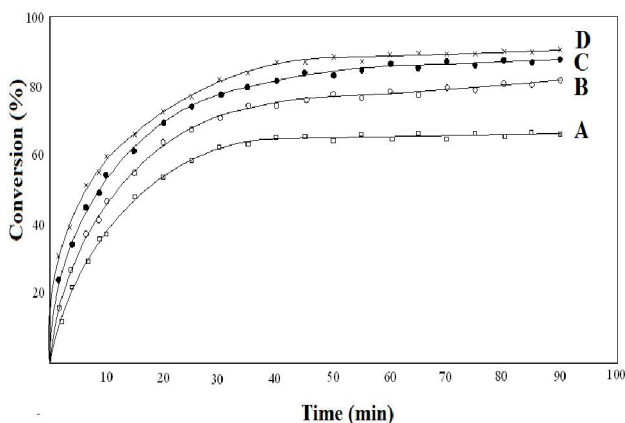

Fig. (5): Conversion – time plot of the emulsion polymerization of VAc in presence of KPS /AcSBS as a redox initiation system using different concentrations of PVA.

A-0.72× 10^{-4}(M)   B-0.612× 10^{-4} (M)
C-0.54× 10^{-4} (M)   D-.36× 10^{-4} (M)

Effect of monomer concentration on the rate of polymerization

Figures (9&10) show the conversion–time relationships for emulsion polymerization of VAc at $50C^0$ using different concentrations of VAc, in presence of KPS/AcSBS, KPS/BSBS in presence of PVA. The rate of polymerization increased with increasing monomer concentration. Figures (11&12) shows give the relationship between the log rates of polymerization versus the log monomer concentration. The rate of polymerization (Rp) was found to be dependent on the concentration of VAc to the powers 0.36 and 0.39.

The rate equation with respect to the monomer:

$$Rp \propto [M]^z$$

Where [M] is the monomer concentration and Z equal 0.36 and 0.39

In our studies the proposed rate equations for the emulsion polymerization of vinyl acetate in presence of PVA as nonionic emulsifier are as follows
in case of KPS/AcSBS and PVA
$$Rp \propto [I]^{1.00} [E]^{1.00} [M]^{0.36}$$
in case of KPS/BSBS and PVA
$$Rp \propto [I]^{0.57} [E]^{0.70}[M]^{0.39}$$

Where {I}, {E}, {M} are initiator, emulsifier and monomer concentration respectively.

Calculation of the activation energy

The activation energies (Ea) for the emulsion polymerization of VAc using KPS/AcSBS and KPS/BSBS as two developed redox initiation systems and pluronic as non ionic surfactant was estimated . From figures(13&14), it is obvious that the conversion percent increase in the rate of flux of radicals, consequently increases the rate of diffusion of radicals into the solublized monomer droplets and as a result the Rp and the maximum conversion increase. Also the log rate vs. 1/T is represented in Figure (15&16). The values of Ea obtained for the different redox initiation systems and non ionic surfactant 2.486 x 10^4 and 5.19 x10^4 J / J/mol for PVA. This result are agree with that obtained by Shaffie et al [18] which stated that the emulsion polymerization of VAc using redox initiation systems composed of different persulphate cations such as sodium persulphate, potassium persulphate and ammonium persulphate, each one coupled with AcSBS. They found that activation energy were 0.84x 10^4 , 1.92x10^4 and 6.68 x10^4 j/mol.

Morophology of the obtained polymer particle

Figure (17) shows the morphology of the obtained latex particles for the emulsion polymerization of VAc prepared using different concentration of the KPS/AcSBS and constant concentration of PVA. Table (1) shows the particle size $\overline{D}_v$ and the polydispersity $\overline{D}_w/\overline{D}_n$, it is obvious that increasing the concentrations of the KPS/AcSBS decreasing the size of the polymer particles values. The greater the number of Nt the better the film forming properties of the obtained latexes which means good application in surface coatings. Also the polydispersity values for the emulsion prepared were founded to be closely equal to 1. i.e. monodisperse emulsion latexes. The graph obtained from TEM for such latexes reveal that the used redox initiation system produced more spherical emulsion latexes particles. Whoever, by increasing the concentration of PVA at constant concentration of AcSBS, the particle size increased. These results are agree with that obtained by Suzuki et al [8,9] who studied the effect of different concentration of PVA on the emulsion polymerization of VAc. They found that lower concentration of PVA give smaller particle diameter.

Mechanism of the reaction

$$X-\underset{\underset{OH}{|}}{\overset{\overset{Y}{|}}{C}}-SO_3^- + S_2O_8^{-2} \longrightarrow SO_4^{-2} + SO_4^{\cdot-} + X-\underset{\underset{OH}{|}}{\overset{\overset{Y}{|}}{C}}-SO_3^{\cdot}$$

Initiation

$$X-\underset{\underset{OH}{|}}{\overset{\overset{Y}{|}}{\overset{\cdot}{C}}}-SO_3 + M \longrightarrow X-\underset{\underset{OH}{|}}{\overset{\overset{Y}{|}}{C}}-SO_3-\overset{\cdot}{M}$$

Propagation

$$X-\underset{\underset{OH}{|}}{\overset{\overset{Y}{|}}{C}}-SO_3-\overset{\cdot}{M} + M \longrightarrow X-\underset{\underset{OH}{|}}{\overset{\overset{Y}{|}}{C}}-SO_3-M-\overset{\cdot}{M}$$

$$X-\underset{\underset{OH}{|}}{\overset{\overset{Y}{|}}{C}}-SO_3-M_{(x-1)} + M \longrightarrow X-\underset{\underset{OH}{|}}{\overset{\overset{Y}{|}}{C}}-SO_3-\overset{\cdot}{M_x}$$

Termination

$$X-\underset{\underset{OH}{|}}{\overset{\overset{Y}{|}}{C}}-SO_3-\overset{\cdot}{M_x} + \overset{\cdot}{M_y}-SO_3-\underset{\underset{OH}{|}}{\overset{\overset{Y}{|}}{C}}-X$$

$$X-\underset{\underset{OH}{|}}{\overset{\overset{Y}{|}}{C}}-SO_3-M_{(x+y)}-SO_3-\underset{\underset{OH}{|}}{\overset{\overset{Y}{|}}{C}}-X$$
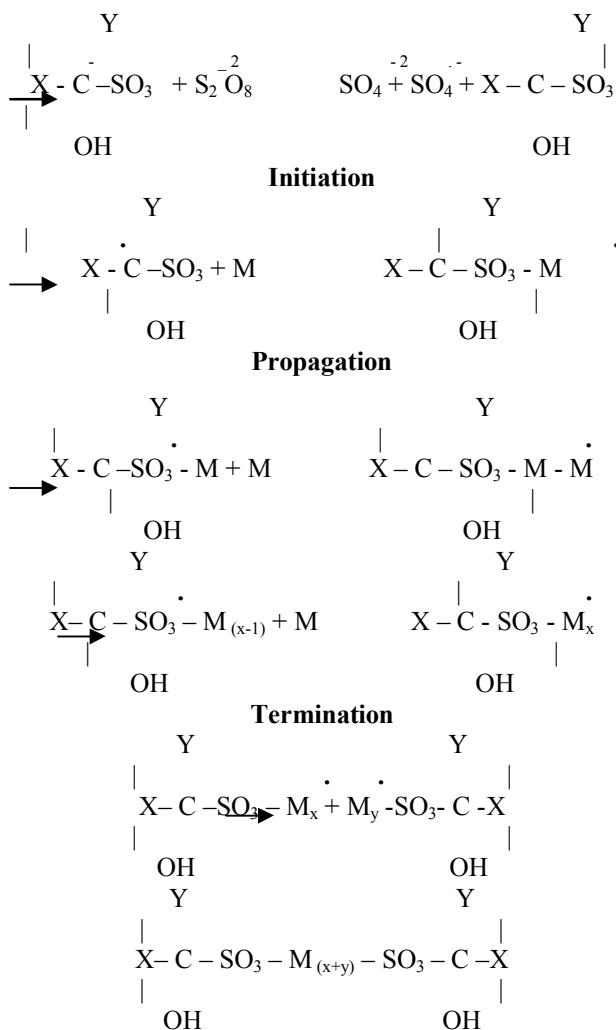
Scheme 1

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