Chapter 2

Experimental

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2.0 EXPERIMENTAL

2.1 Introduction

Introduced in 1953, acrylic resin emulsions are generally noted for their toughness, out door durability and good adhesion to a wide variety of surfaces. Hence, the monomers methyl methacrylate and butyl acrylate were chosen for the work, as one of the objectives was to study the relevance of microemulsion polymerization to surface coatings.

Large number of surfactants nonionics and ionics were examined for microemulsion formulations. The oil used was the monomer itself. Non-ionics studied were Noigen NP 6 (nonyl phenol ethylene oxide condensate with 6 units of ethylene oxide) and Hyoxyd AAO (ethylene oxide 10 units). Cationics studied were cetyl trimethyl ammonium bromide and cetyl pyridinium chloride and anionics were sodium dioctyl sulfosuccinate, sodium dodecyl benzene sulphonate and sodium dodecyl sulphate. The non-ionics did not form o/w microemulsions. The ionic surfactants could form microemulsions. However, cationic surfactants were not used for further study as most latex vehicles used in paint formulations are stabilized with anionic surfactants which will be neutralized by the cationics resulting in destabilization and coagulation of the latex[1]. Among anionics studied, for o/w microemulsion sodium dodecyl sulphate and disodium diphenyl oxide disulphonate (Dowfax 2A-1) gave the best result.

2.2 Reagents and Chemicals

Acetone	Qualigen, Glaxo, India.
Acrylamide	Sisco Chem, India.

Ammonium persulphate (APS)	Sisco Chem, India.
2,2'-Azo bis isobutyronitrile (AIBN)	Sisco Chem, India.
Benzoyl peroxide (BPO)	Fluka, Switzerland
Butyl acrylate (BA)	BDH, India
Calcium Chloride (fused)	Qualigen, Glaxo, India.
Chloroform	Qualigen, Glaxo, India.
Dowfax 2A-1	Dow Chem, U.S.A.
Hydroquinone	E. Merck, Germany.
Potassium persulphate (KPS)	Sisco Chem, India.
Methanol	Qualigen, Glaxo, India.
Methyl methacrylate (MMA)	Sisco Chem, India.
2-Pentanol	Sisco Chem, India.
Sodium dodecyl sulphate (SDS)	Qualigen, Glaxo, India.
Sodium hydroxide	Sisco Chem, India.
Tetrahydrofuran	Qualigen, Glaxo, India.
Uranyl acetate	E. Merck, Germany.

2.3 Purification of Monomers and Chemicals

Methyl methacrylate and butyl acrylate were extracted with 5 % sodium hydroxide solutions, to remove the inhibitor and then with distilled deionised water to remove sodium hydroxide. After drying over fused calcium chloride, the monomers were vacuum distilled under nitrogen. The purified monomer were stored at 4°C.

2,2'-Azo bis isobutyronitrile was recrystallized twice from methanol and benzoyl peroxide from chloroform.

All other chemicals and solvents used in the work were of high purity and hence further purification was not done. Attempts were made to ensure that all the glasswares were scrupulously clean and all transfer operations were performed with uniformity at all stages. All the experimental procedures were performed in duplicate to ensure the reproducibility. The samples given for the instrumental analysis were ensured to be in the most suitable forms.

2.4 Phase diagram

The clear (transparent) region for oil/water microemulsion was determined visually by titrating oil against deionised water containing known amount of sodium dodecyl sulphate in a screw capped tube at 27°C. The oil used was methyl methacrylate, butyl acrylate and 1:1 (w/w) mixture of methyl methacrylate and butyl acrylate. The clear turbid boundaries were established from systematic titrations.

2.5 Synthesis (batch method)

Methyl methacrylate and butyl acrylate homopolymers and copolymers were synthesized by batch processes from microemulsion and emulsion media using sodium dodecyl sulphate.

2.5.1 Synthesis of Poly (methyl methacrylate)

For the synthesis of poly (methyl methacrylate), purified methyl methacrylate 9.9%, sodium dodecyl sulphate 14.0% and water 76.1% by weight were taken in a 5 neck reaction kettle. The mixture was stirred to form optically transparent, isotropic and thermodynamically stable microemulsion. The reaction vessel was equipped with a thermometer and water condenser and the reaction mass was stirred mechanically. The temperature of the reaction mixture was maintained at 80°C with an accuracy of ± 0.5°C. At 80°C, 1.25×10^{-3} M (0.26 % based on monomer) potassium persulphate, dissolved in minimum volume of water, was added to the reaction mixture. The reaction was allowed to continue for two hours and then the reaction mixture was poured into four fold excess of methanol with constant and vigorous stirring. The precipitated polymer was filtered, washed with methanol and dried in vacuum at 60°C to constant weight. PMMA was also synthesized from emulsion medium. The composition of the emulsion was monomer 11.4 %, SDS 0.9 %, and water 87.7 % by weight. All other conditions were similar to those mentioned earlier for microemulsion polymerization.

2.5.2 Synthesis of Poly (butyl acrylate)

Poly butyl acrylate was synthesized at the same experimental conditions as mentioned earlier for PMMA. The composition of the polymerizing recipe was also similar to that mentioned in section 2.5.1 for PMMA synthesis, except that MMA was replaced by butyl acrylate in the microemulsion and emulsion composition.

2.5.3 Synthesis of Poly (methyl methacrylate-co-butyl acrylate)

Poly (methyl methacrylate-co-butyl acrylate) was synthesized at the similar experimental conditions as mentioned earlier for PMMA. The composition of the recipe contained 9.9% MMA-BA (1:1 w/w) for microemulsion system and 11.4% MMA-BA (1:1 w/w) in emulsion system. Concentration of other components was same as that used in the polymerization of MMA.

2.6 Optimization of reaction conditions for copolymerization in microemulsion medium

As our main interest is in copolymers of MMA and BA we have not studied in detail optimization of various conditions for PMMA or PBA synthesis. However, kinetics of these reactions was studied in detail. But optimization of reaction conditions was done for methyl methacrylate and butyl acrylate copolymers by varying the initiator type and concentration, temperature, cosurfactant concentration, monomer concentration and time.

2.6.1 Initiator type and concentration

The influence of type of initiator and its concentration on the copolymerization of MMA and BA was studied by performing the polymerization in the microemulsion medium (water 76.1%, SDS 14.0% and monomer 9.9% w/w). The free radical initiators examined over 0.1×10^{-3} M to 1.25×10^{-3} M, concentration based on water, (~0.02% to ~0.26% with respect to monomer), were ammonium persulphate, potassium persulphate, azo bis isobutyronitrile and benzoyl peroxide.

2.6.2 Temperature

The effect of temperature on the copolymerization of the earlier mentioned microemulsion was studied by using 1.25×10^{-3} M potassium per sulphate and benzoyl peroxide (0.26% KPS and 0.23% benzoyl peroxide with respect to monomer) over 70°C - 90°C.

2.6.3 Cosurfactant concentration

Till 1990, it was believed that for the formation of microemulsion use of cosurfactant is must. However, in 1990 Perez-Luna et al[2] reported that microemulsion exist without cosurfactant. Hence we have tried to examine the role of cosurfactant in the microemulsion polymerization. The effect of 2-pentanol as a cosurfactant in the microemulsion recipe was studied by using 0.83% and 1.66 % concentrations of it in the recipe containing 76.7% water, 10.0 % MMA-BA (1:1 w/w) and 13.3% SDS. Potassium persulphate at 1.25 x 10^{-3} M based on water (0.26% with respect to monomer) was used for the initiation and the polymerization was carried out at 80°C.

2.6.4 Monomer Concentration

The effective monomer concentration[3] was considered to be 100 x [Monomer] / [Monomer] + [Surfactant]. Keeping the monomer concentration constant at 6 gm, water 46.2 gm and varying sodium dodecyl sulphate from 0.5 gm to 14.0 gm it was observed that when effective monomer concentration was between 92.3% to 42% the systems were in emulsion form. Below 42% monomer concentration, the system existed in a single phase. The monomer concentrations used in the study were 92.3%, 60.0%, 41.4% and 30.0% and polymerization was carried out by using 1.25 x 10^{-3} M KPS at 80° C.

2.6.5 Time

The effect of reaction time on the rate of polymerization was studied at 80°C using 1.25 x 10^{-3} M KPS (0.26 % with respect to monomer) concentration. The rate was determined by withdrawing 5 ml of the reaction mixture at different time intervals and arresting the reaction by adding 20 ppm of hydroquinone and precipitating the polymer with methanol. Percentage conversion was calculated gravimetrically.

2.7 Kinetic of methyl methacrylate polymerization in emulsion and microemulsion media

Kinetic study of methyl methacrylate polymerization in emulsion and microemulsion was performed by varying reaction conditions such as temperature, initiator concentration, and monomer concentration. Monomer concentration was taken as 100 x [Monomer] / [Monomer] + [Surfactant]. The composition of the polymerizing recipe was same as mentioned in section 2.5.1. The reaction was carried out under nitrogen atmosphere. The rate of polymerization was determined by withdrawing 5 ml of the reaction mixture at different time intervals and arresting the reaction by adding 20 ppm of hydroquinone and precipitating the polymer with methanol. Percent conversion was calculated gravimetrically.

2.7.1 Temperature

The rate of reaction depends on the temperature. Hence the effect of reaction temperature on the kinetics of polymerization of MMA was studied for the microemulsions and emulsions mentioned earlier, using 0.5×10^{-3} M KPS (0.10% based on monomer) at different temperatures. The polymerization kinetics was studied at 70°C, 80°C and 90°C.

2.7.2 Initiator concentration

Free radical polymerization requires optimum concentration of initiator. Hence, the effect of initiator concentration on the rate of polymerization of MMA was studied by initiating the earlier mentioned microemulsions and emulsions at 80°C using different concentrations of potassium persulphate ranging from 0.1 x 10^{-3} M to 1.25 x 10^{-3} M (0.02% to 0.26% based on monomer).

2.7.3 Monomer concentration

The effect of monomer concentration 100 x [Monomer] / [Monomer] + [Surfactant] on the rate of polymerization was studied by initiating the earlier mentioned microemulsions and emulsions at 80°C using 1.25 x 10^{-3} M KPS (0.26%) concentration and varying monomer concentrations.

2.8 Kinetic study of polymerization of butyl acrylate and copolymerization of methyl methacrylate and butyl acrylate.

Kinetics of the polymerization of butyl acrylate and copolymerization of methyl methacrylate and butyl acrylate was also studied as discussed for MMA in section 2.7.

The emulsion and microemulsion compositions used for polymerization are summarized below :

Table 2.1 : Recipes for microemulsion systems

	MMA	BA	MMA-BA (1:1 w/w)	% Composition
Water (gms)	92.4	92.4	92.4	76.1
Monomer (gms)	12.0	12.0	12.0	9.9
SDS (gms)	17.0	17.0	17.0	14.0

In emulsions only difference was in the concentration of SDS which was 1·0 gm. This resulted in composition of 87.7% water, 11.4% monomer and 0.9% SDS, for emulsion.

2.9 Semicontinuous microemulsion copolymerization of methyl methacrylate and butyl acrylate

Polymerization was carried out in a 5-neck 500 ml reaction kettle, equipped with a reflux condenser, teflon blade stirrer, sampling device, nitrogen inlet and a feed inlet tube, in nitrogen atmosphere. The micellar solution containing ~90% of surfactant with respect to the total surfactant in the recipe was charged into the reactor and heated to 80°C. The initiator dissolved in minimum quantity of water was added just before the feed flow was started. The feed containing ~10% of the surfactant with respect to the total surfactant in the recipe and whole of the monomer MMA-BA (1:1) and 25% water with respect to total water in the recipe was vigorously stirred to form emulsion. This was then added at constant flow rate to the reactor. The polymerization was continued thereafter in batch for one and half hours.

2.9.1 Semicontinuous polymerization using Disodium diphenyl oxide disulphonate (Dowfax 2A-1)

As disodium diphenyl oxide disulphonate (Dowfax 2A-1) has not been used for the batch process due to the paucity of the surfactant, optimization of the conditions for the copolymerization of MMA and BA by semicontinuous method was done and is discussed here. The composition of studied reactions are given in Table 3.19.

(i) Surfactant concentration

The surfactant concentration was varied between 1.7 to 5.8% of total composition of the recipe. The reaction was carried out at 80°C with monomer concentration around 30% and water ~65%. Ammonium persulphate initiator was used at 0.3% concentration with respect to monomer (0.15% with respect to total composition).

(ii) Monomer concentration

The monomer concentration in the total composition as described earlier was varied between 30% to 50% and reaction was carried out at 80°C using ammonium persulphate initiator at 0.3% concentration with respect to monomer.

(iii) Cosurfactant type

The effect of cosurfactant acrylamide and pentanol on copolymerization of MMA and BA was studied at 80°C keeping monomer concentration around 40% and water at 55%. Ammonium persulphate initiator was used at 0.3% concentration with respect to monomer.

(iv) Initiator type and concentration

Various types of initiators such as ammonium persulphate, potassium persulphate, azo bis isobutyronitrile and benzoyl peroxide were used for polymerization at 80°C temperature. Based on the results obtained ammonium persulphate was selected for the further work.

The effect of ammonium persulphate concentration was studied by varying the initiator concentration from 0.05 to 1.44% with respect to monomer at 80°C. Experiments were performed with and without acrylamide as a cosurfactant. The monomer concentration was kept at 40% and water at 55%.

(v) Temperature

The effect of temperature on the polymerization was studied by polymerizing the recipe surfactant 3.7%, monomer 40.4%, acrylamide 0.4%, water 55.4% and ammonium persulphate 0.3% with respect to monomer at 70°C, 80°C and 90°C. Polymerization was also carried out without cosurfactant, acrylamide, at the above temperatures.

2.9.2 Semicontinuous polymerization using sodium dodecyl sulphate

Microemulsion copolymerization of methyl methacrylate and butyl acrylate in a semicontinuous manner was carried out mainly using two anionic surfactants namely sodium dodecyl sulphate and disodium diphenyl oxide disulphonate (Dowfax 2A-1).

From the phase diagram of SDS/Water/(MMA-BA 1:1 w/w) a composition was chosen in which the SDS/monomer (w/w) ratio was 1.42. The polymerization of the recipe containing water 76.1%, SDS 14.0% and monomer 9.9% at 80°C was carried out. Polymerization was also carried out by decreasing SDS/monomer ratio from 1.42 to 0.38 to achieve latexes with higher polymer/surfactant ratios. The monomer/initiator ratio was kept constant.

Optimization of reaction conditions in semicontinuous method using SDS was not done as it is has been extensively studied by batch process.

2.10 Characterization of Polymers

Products synthesized by homopolymerization of MMA and BA and copolymerization of MMA and BA were characterized by the following methods.

2.10.1 Infra Red spectrometry

IR spectroscopic analysis of the polymer films was done on Perkin-Elmer 960 (4000 cm^{-1} - 650 cm^{-1}) spectrophotometer.

2.10.2 Nuclear Magnetic Resonance spectrometry

High resolution ^1H and ^{13}C NMR of the polymers were recorded on Bruker NMR spectrophotometer at 500 MHz using $CDCl_3$ as solvents.

2.10.3 Gel Permeation Chromatography

The GPC analysis was carried out on Water's GPC 150 C instrument. The columns used were Waters μ-styragel with porosity 10^5, 10^4, 10^3, 500 and 100A°. Eluent was tetrahydrofuran and the rate of flow was 1.0 ml/min. RI detector and PMMA of different molecular weights as standard was used for calibration. From the chromatogram, molecular weight distribution along with weight average and number average molecular weights were obtained.

2.10.4 Thermal Analysis

(i) Thermo gravimetric analysis (TGA)

The thermogravimetric analysis of all the polymers were carried out on the Shimadzu DT 30 thermal analyzer. The samples were weighed into platinum sample pans and heated at the rate of 10°C/minute. All the measurements were made under nitrogen atmosphere at a flow rate of 50 ml/minute.

(ii) Differential Thermal Analysis (DTA)

Differential thermal analysis of the polymers were carried out at 10°C/minute heating rate in nitrogen atmosphere using a Seiko Instruments SSC/5200 thermal analyzer.

(iii) Differential Scanning Calorimetry (DSC)

The differential scanning calorimetric analysis of the polymers was carried out on Mettler DSC TJ-4000 thermal analyzer. Samples were heated at 10°C/minute in the range of 25°C to 500°C in nitrogen atmosphere.

2.10.5 Viscometry

Viscometric studies of polymers in acetone were carried out at different temperatures using an ubbelohde internal dilution viscometer. The viscometer was fitted with a sintered glass filter in order to prevent any undissolved polymer or dust agglomerates from entering the capillary. The viscometer was clamped in an upright position in a large thermostated waterbath maintained at a desired temperature with an accuracy of ±0.50°C. The solvent flow times were measured with 15 ml of the solvent. The time (t_o) required for the meniscus to fall between the two etched marks was recorded. Measurements were repeated until the readings were constant. Similar procedure was used to measure the flow time (t) of accurately assembled polymer solutions. The solutions were given sufficient time to equilibrate to the required temperature.

Viscosity measurements were also done in θ-solvent. θ-solvent of the individual polymer at a particular temperature was determined by varying the solvent and non-solvent composition at that temperature.

2.11 Characterization of microemulsion latexes

2.11.1 Absorption spectrometry

Light transmission through microemulsion latexes was studied using Shimadzu 2000 UV-visible spectrophotometer.

2.11.2 Particle size analysis

(i) Transmission Electron Microscopy

Average particle size of the polymerized microemulsion latexes was determined using JEOL JEM 100 SX Transmission electron microscope. A drop of polymerized latex was added to 2 ml of 2 % uranyl acetate solution. One drop of this diluted latex was put on a copper grid which was coated with thin layer of formvar. Average particle size was calculated considering 100 particles per 25 cm^2.

(ii) Particle size analyzer

Median diameter and particle size distribution in polymerized microemulsion latexes were determined by using Brookhaven B 90 (USA) particle size analyzer and Shimadzu Sald 2001 Particle Size Analyzer.

2.11.3 Viscosity

Brookfield digital viscometer model LVTD serial A 03379 was used to determine the viscosity of the microemulsion latexes as per the procedure mentioned in ASTM D 2196-86.

2.11.4 Mechanical Stability

Dispermat F 105 was used to determine the mechanical stability of the microemulsion latexes. 100 gm of microemulsion was taken in a stainless steel container and stirred at 14000 r.p.m. for 10 minutes. The microemulsion was then strained through the 100 mesh nylon cloth and the grit content was determined gravimetrically.

2.11.5 Electrolytic Stability

To 100 gm of microemulsion latex 5 % solution of aluminum sulphate was added with stirring till the microemulsion was completely coagulated. The volume of $Al_2(SO_4)_3$ solution required for complete coagulation was recorded.

2.11.6 Freeze-thaw Stability

Microlatexes can suffer freezing during storage, and therefore resistance to freeze-thaw cycle is important for commercialization. In order to measure the freeze-thaw stability, the latexes were subjected to cycles where the samples were frozen at -10°C for 24 hours and then allowed to thaw at room temperature for another 24 hours. Both, the amount of coagulum formed and the increase of particle size were taken as a measure of the freeze-thaw stability. The cycles were repeated to note the number of freeze-thaw cycles the latex can endure.

2.12 Film characterization

The microemulsion latex films of 150 μm thickness were casted on glass panels and allowed to dry for 48 hours at 28°C - 30°C. The film was then studied for its clarity, presence of bits, adhesion (tackiness), water resistance and alkali resistance.

2.12.1 Water Resistance

The water resistance of microemulsion films was determined as follows : The dried films were dipped in deionised water at room temperature. The water resistance after one, two, four and twenty-four hours was recorded with rating 10 for excellent and 5 for poor water resistance, which is examined through haziness developed.

2.12.2 Alkali Resistance

The microemulsion films of 150 µm thickness were dipped in 5% sodium hydroxide solution. The weight of the glass panel without film and along with dried film was recorded before being dipped in alkali solution. After 24 hours, the glass panel was taken out, dried and weighed. Weight loss was calculated from the results. Haziness, or blisters or any change in physical property was also noted.

2.13 Paint Formulation

Proper paint-formulation techniques are just as important as the choice of the type of emulsion in getting desirable film properties. The process involves pigment dispersion followed by the addition of emulsifier and other additives, adjustment of pH, viscosity and tinting.

Two common recipes designed to have low viscosity (~50% water) and high viscosity (~25% water) were used for paint formulations. The dispersing and wetting agents, coalescent, antifoamer, thickener and water were charged and mixed. The pigments and extenders were then added, mixed until all aggregates were broken down and were homogeneously dispersed with Sri Ram Turbo disperser, a high speed disperser. At this finish was checked.

After this, the dispersed pigment paste, which is also known as mill base, was diluted by adding the emulsion vehicle, defoamer and additional water or thickener as necessary to adjust viscosity. Mixing continues at a low speed until the paint batch is thoroughly blended. Finally the pH of the finished latex paint is adjusted if necessary.

The paint preparation was carried out at R & D center, Asian Paints at Bombay.

The details of the paint formulation are in section, 3.12

2.14 Characterization of Paint Formulation

2.14.1 Viscosity

Due to the variation in the viscosities of the paint formulation based on SDS and Dowfax 2A-1, Penetrometer and Thomas Stormer viscometer were used for the measurements of the viscosities as per the requirements.

(i) Penetrometer

The viscosities of distempers, coaltar paints and other stiff paints are generally determined by using penetrometer. Higher divisions on penetrometer indicate lower viscosity. The scale is DOP i.e. divisions on penetrometer. The paint formulations based on Dowfax 2A-1 microemulsions, were stiff in nature hence Penetrometer AIMIL model 512 was used to determine the viscosities of the formulated paints.

(ii) Stormer viscometer

Stormer viscometry is suitable for the measurements of comparatively lower viscosity materials such as emulsion paints, emulsions and mill bases. Viscosities are expressed in krebs unit. The viscosity of paint formulation based on SDS and standard emulsion was determined using Thomas Stormer Viscometer 9730 F 10 model as per the ASTM 06 01 D562-89 procedure.

2.14.2 Colour Intensity

The microemulsion based paints were tested for colour intensity as follows : Two grams of Apcolite universal stainer fast blue (from Asian Paints, Bombay) was added to 100 gms of paint formulation and mixed thoroughly. The colour intensity was determined on Colour Computer ACS (applied color systems inc.) model CS3.

2.14.3 Stain Resistance

The microemulsion paint was applied on glass panels and dried for 48 hours at 28-30°C and stained with a 30% solution of gilsonite in mineral turpentine. After staining the film was immediately washed with excess of mineral turpentine and wiped with tissue paper. The extent of black stains on paint film was then recorded with ratings 10 for maximum stain resistance and 5 for minimum.

2.14.4 Scrub Resistance

The microemulsion paint was applied on black scrub panels 16 X 42 cms with 150 microns applicator. The film was dried for 7 days at 28°C to 30°C. The wet scrub resistance was determined with Erichsen Washability and Scrub Resistance Tester model 494 as per ASTM 06 01 D4213-92.

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