

Experimental Studies on *n*-Octane and Cyclohexane as Organic Solvent for Synthesis of Polyurea Microcapsules by Interfacial Polycondensation

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Abstract - Interfacial polycondensation (IP) is one of the most important step polymerization technique used for synthesis of polyurea microcapsules. IP reaction between diamine and diisocyanate monomers which are soluble in aqueous phase and organic phase respectively is very fast therefore the overall process of polyurea synthesis via interfacial polycondensation, by and large, mass transfer controlled reaction. Selection of proper organic solvent is one of the important parameter for IP reactions. The objective of this experimental work was to study the effect of *n*-Octane and Cyclohexane as an organic solvent on kinetics of polyurea microcapsules synthesized by interfacial polycondensation reaction. In this reaction system IP reaction occurs on organic side of the interface so reaction rate increased with increase in relative polarity of organic solvent. Characterization of polyurea was carried out by XRD and DSC which demonstrated that semi crystalline polyurea microcapsules with good thermal stability were synthesized.

Keywords - Interfacial Polycondensation, *n*-Octane, Cyclohexane, Polyurea, Polymerization

1. Ionic equilibrium for the aqueous phase monomer (monomer A).
2. Transport of the aqueous phase monomer (monomer A) and/or the organic phase monomer (monomer B soluble in organic solvent) from bulk phases to the site of reaction
3. Reaction between the two monomers.
4. Phase separation of the formed oligomeric species. [5]

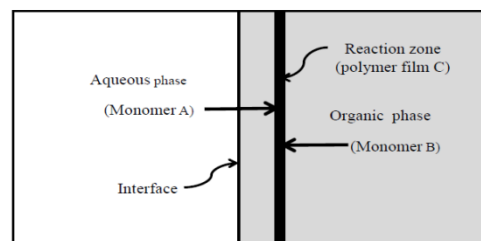


Fig. 1 Schematic diagram of interfacial polycondensation

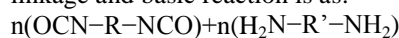
I. INTRODUCTION

Interfacial Polycondensation is a step polymerization technique which is effectively applicable for synthesis of polyamide, polyester, polycarbonate, polyurea and polyurethane polymers [1]. Microencapsulation of an active ingredients (AI) using these polymers is one of the key applications, both monocoresh type and matrix type microcapsules are produced by IP, depending on the solubility of the polycondensate in the droplet phase [2].

During encapsulation with interfacial polycondensation, monomers in their respective phases diffuse onto the oil-water interface where they react with each other to form a polymer surrounding the droplets. Usually, the water-soluble monomer can participate in both the aqueous and the oil phases, while the oil-soluble monomer can only be dissolved in the oil phase. Therefore, the membrane thickness grows towards the oil phase [3]. When the initial membrane is formed, the water-soluble monomer has to diffuse across the membrane into the oil phase to react with the oil-soluble monomer to thicken and to strengthen the membrane. The increment of the membrane thickness depends on both the diffusion of the monomers and the reaction between the monomers [4]. Fig. 1 shows schematic diagram of IP reaction, IP reaction proceeds as per following steps

Monomer concentration, concentration and type of emulsifier used, nature and type of organic solvent, volume ratio of dispersed phase to continuous phase, different types of surfactants, and speed of agitation were important parameters reported in literature which govern the reaction kinetics of IP reactions. [2, 4] Selection of the organic solvent is important parameter for IP reaction kinetics since it will affect several other polycondensation factors such as the partition coefficient of the reactants between the two phases, the diffusion of the reactants, reaction rate, and the solubility, swelling, or permeability of the growing polymer. [6] In general, highly aqueous phase immiscible organic solvents (in which one of the monomer is maximum soluble) are applicable for IP. Table-1 shows different organic solvents reported in literature for polyurea synthesis via IP.

In this experimental work, basic reaction of polyurea synthesis was considered as a step growth polycondensation reaction between hexamethylene-1, 6-diamine (HMDA) and hexamethylene-1, 6-diisocyanate (HMDI) to form a urea linkage and basic reaction is as:



Effect of two different organic solvents i.e. *n*-Octane and Cyclohexane, on reaction kinetics of polyurea synthesis by IP was studied.

TABLE I DIFFERENT ORGANIC SOLVENT STUDIED IN LITERATURE FOR SYNTHESIS OF POLYUREA BY IP

Organic Solvent	Aqueous Phase Monomer	Organic Phase Monomer	Reference
Xylene, Cyclohexane	Diethylene Triamine	Poly methyl Polyphenyl Isocyanate (PMPI)	[7]
P-Xylene, Cyclohexane	Tetraethylene Pentaamine	Polymethyl Polypheny Isocyanate (PMPI)	[8]
Cyclohexane	Ethylene Diamine	Toluene 2,4- Diisocyanate (TDI)	[9]
Cyclohexane	Lysine	Toluene 2,4- Diisocyanate (TDI)	[4]
P-Xylene, Cyclohexane, Toluene, Carbon Tetra chloride	Hexamethylene-1,6Diamine (HMDA)	Hexamethylene-1,6 Diisocyanate (HMDI)	[5]
Toluene	Hexamethylene-1,6Diamine (HMDA)	4,4'-Methylenebis (Phenyl Isocyanate)	[10]

II. EXPERIMENTAL

A. Materials

Hexamethylene-1, 6-diamine (HMDA) and hexamethylene-1, 6-diisocyanate (HMDI) of purity >99% were obtained from Sigma-Aldrich, USA. Both were used without further purification. The emulsifier Tween-85 (Sigma-Aldrich, USA) was used to stabilize the o/w emulsions in which the reaction was carried out. The organic solvents n-Octane and Cyclohexane were purchased from S D fine chemicals Ltd. India.

B. Methods

The polyurea microcapsules were synthesized by interfacial polycondensation of Hexamethylene-1, 6-diamine (HMDA) and hexamethylene-1, 6-diisocyanate (HMDI) according to the procedure reported in the literature [11, 12].

A two- step procedure is adopted and total volume of aqueous phase is constant in all experiments. In first step oil- water emulsification was carried out at 3000RPM using high speed emulsifier. Phase volume ratio (V_d/V_c) i.e. ratio of volume of dispersed phase (V_d) to volume of continuous phase (V_c), was 0.05 constant for all experiments. In second step, appropriate emulsion was added to an aqueous solution of HMDA and was continuously stirred at 200 RPM. Cyclohexane and n-Octane were used as solvent for organic phase monomer HMDI. Reaction was carried out at constant temperature of 25 °C. As the reaction was very fast continuous drop of pH was direct measure of rapid change of concentration of HMDA which was accurately measured using advanced PLC based pH Logger. Values of other reaction parameters i.e. initial mole ratio of the monomers, R and number of moles of limiting monomer per unit volume of dispersed phase, n_L/V_d were selected as 1.2, 2.4 and 0.36, 0.72 respectively.

C. Characterization

The powder X-ray analysis of polyurea samples was recorded using Bruker powder X-ray diffractometer (Model D2 Phaser, Bruker, USA). Percentage crystallinity was calculated from X-ray diffractogram using ORIGIN-85.TGA/DTA1 METLER TOLEDO was used to evaluate thermal stability of polyurea in the range of temperature 30°C to 500°C at a heating rate of 10°C/min.

III. RESULTS AND DISCUSSION

A. Effect of n-Octane and Cyclohexane on Reaction Kinetics of Polyurea Synthesis by IP:

As shown in Fig. 2 declination in pH of an aqueous phase indicates drop in concentration of HMDA i.e. aqueous phase monomer for constant value of R (initial monomer concentration ratio), n_L/V_d (number of moles of limiting monomer per unit volume of dispersed phase), phase volume ratio (V_d/V_c) and temperature (T), polyurea was synthesized via IP using n-Octane and Cyclohexane as organic solvent. Kondo et. al. stated that an organic solvent in which the aqueous phase monomer is able to partition better would give higher rates than one in which the partitioning is poorer. Further, the intrinsic kinetics of polymerization could influence the rate of phase separation and the structure of the film that forms, and there could therefore raise an indirect influence on the observed rate of IP [13].

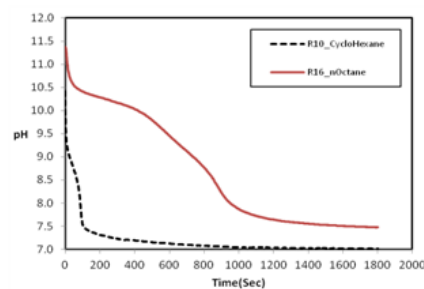


Fig. 2 Effect of organic solvent on reaction kinetics of IP (other conditions R=2.4, $n_L/V_d=0.36$, T=25°C, $V_d/V_c=0.05$)

There is a noticeable difference in the rate of reaction for the two solvents used. The reaction rate is higher for Cyclohexane than for n-Octane for the same other conditions. As discussed in literature, unlike other organic reactions, IP reaction is also influenced by change in relative polarity of organic solvent and hence its charge density. Figure 3 represent similar behavior of reaction kinetics of IP reaction carried out with use of n-Octane and Cyclohexane as organic solvents with variation in bulk monomer mole ratio (R) from 2.4 to 1.2.

A dielectric constant value of Cyclohexane is 2.02 and that of n-Octane is 1.93. Solvent polarity is directly related with its dielectric constant so Cyclohexane is more polar

compare to *n*-Octane on the basis of ratio of polarity of solvent to that of water (considered as relative polarity), Cyclohexane has a relative polarity 0.006 and *n*-Octane has 0.015 [14]. From reported kinetics of IP reactions in literature, as relative polarity increases reaction rate decreases. In this experimental work we also confirmed the same. Thus, selection of a proper organic solvent for interfacial polycondensation reaction is an important parameter. The common organic solvents inert and immiscible with water are generally preferred in interfacial polycondensation.[15].

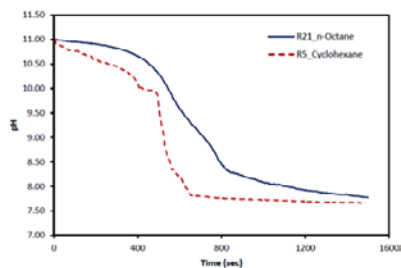


Fig. 3 Effect of organic solvent on reaction kinetics of IP (other conditions $R=1.2$, $n_L/V_d=0.36$, $T=25^\circ\text{C}$, $V_d/V_c=0.05$)

A. XRD Analysis of Polyurea

Fig. 4 shows the XRD of Polyurea sample. A semi-crystalline nature is shown by the diffractogram. The percentage crystallinity was 21.54%.

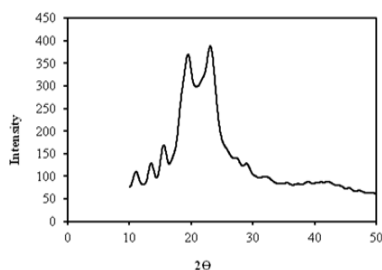


Fig.4 X-ray Diffractogram of polyurea synthesized with *n*-Octane as a solvent

B. DSC Analysis of Polyurea

DSC analysis curve for polyurea sample is shown in Fig. 5. Temperature values of 177.20°C , 223.87°C and 263.98°C are first, second and third peak values considered as melting, decomposition and degradation temperature respectively. It represents that the polyurea has high thermal stability.

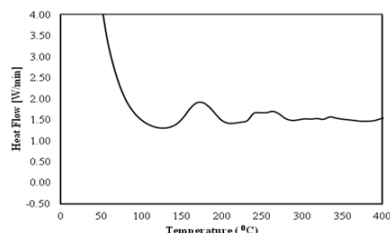


Fig.5 DSC Thermogram of polyurea synthesized with *n*-Octane as a solvent

IV. CONCLUSION

Interfacial polycondensation of oil phase monomer Hexamethylene Diisocyanate (HMDI) and aqueous phase monomer Hexamethylene Diamine (HMDA) is one of the best suitable methods for synthesis of Polyurea microcapsules. Selection of proper organic solvent for organic phase monomer is considered as a key experimental parameter. There is a noticeable difference in the rate of reaction for the two solvents used. The reaction rate is higher for Cyclohexane than for *n*-Octane for the same other conditions. The common organic solvents inert and immiscible with water are generally preferred in interfacial polycondensation. Polarity of solvent is an important variable as the locus of reaction is in the reaction zone which is in the vicinity of the interface towards the organic phase. Relative polarity of organic solvent controls the diffusion of aqueous phase monomer and hence there is an inverse correlation observed in reaction rate and relative polarity of organic solvent. Semi-crystalline structure of polyurea microcapsules with higher thermal stability was obtained with the use of IP method.

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