MECHANISM OF EMULSIFICATION OF STYRENE USING HEXADECYLTRIMETHYLAMMONIUM BROMIDE–CETYL ALCOHOL MIXTURES

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ABSTRACT

Ionic emulsifier–cetyl alcohol mixtures give more stable emulsions than the ionic emulsifiers alone, e.g., the emulsification of styrene using hexadecyltrimethylammonium bromide–cetyl alcohol mixtures gives better stability during emulsion polymerization than ammonium bromide alone. The emulsification of this system was investigated by the conductometric titration of the aqueous mixed emulsifier system at 63° with styrene. At the hexadecyltrimethylammonium bromide–cetyl alcohol ratios which gave good stability, the conductance decreased with increasing styrene concentration to a minimum, then increased to a maximum and decreased slightly or leveled off. During the initial decrease, the sample was translucent and comprised a small number of relatively large (ca. 500 nm) droplets which broke down to form a large number of very small (ca. 130 nm) droplets; beyond the first inflection point, the sample gradually became opaque and the very small droplets coalesced to form a constant number of larger (ca. 200 nm) droplets; beyond the second inflection point, the sample was opaque and the constant number of particles grew in size and narrowed in distribution to form monodisperse (ca. 350 nm) droplets. The initial mixed emulsifier system contained crystalline rod-like particles (1–2 µm length; 0.1–0.2 µm diameter), which disappeared as the relatively large droplets broke down to form very small droplets. With hexadecyltrimethylammonium bromide alone, the conductance decreased to an inflection point, then decreased more slowly thereafter; the sample was translucent before the inflection point and opaque afterwards; no crystalline rod-like particles were observed. These results suggest that the
hexadecyltrimethylammonium bromide and cetyl alcohol form a crystalline complex which disappears as the emulsion droplets are formed, to release hexadecyltrimethylammonium bromide to the aqueous phase, and then reappears on the droplet surfaces as an adsorbed complex of the optimum ratio.

INTRODUCTION

Today, water-based coatings are replacing organic solvent-based coatings because of their environmental and economic advantages1–3. The water-based polymer vehicles can be divided into three classes4: (i) water-soluble polymers, which form solutions of individual hydrophilic polymer molecules; (ii) latexes, which comprise colloidal dispersions of hydrophobic polymer particles, each of which contains hundreds or thousands of polymer molecules; (iii) water-solubilized polymers, which form dispersions intermediate in size and hydrophilic-hydrophobic character between the hydrophilic polymer molecules and the hydrophobic latex particles. The water-soluble polymer solutions are true solutions of polymer molecules; their viscosities depend upon the concentration and molecular weight of the polymer. The latexes are true colloidal sols; their viscosities depend upon the viscosity of the aqueous medium and the interaction between the colloidal particles, and are independent of the polymer molecular weight. The low viscosity, high solids, and high molecular weights of the polymer latexes suits them for application as coatings.

Latexes can be divided into three classes, according to their origin and method of preparation5: (i) natural latexes; (ii) synthetic latexes made by emulsion polymerization; (iii) artificial latexes made by emulsification. Natural latexes are limited to only a few polymer types produced on plantations in tropical areas. Synthetic latexes are available in great variety: the emulsion polymerization process used to make them can be applied to any water-immiscible monomer that can be polymerized by free radical-initiated vinyl addition polymerization, and several latex families — butadiene-styrene and styrene-butadiene copolymers, polybutadiene, polychloroprene, polyvinyl acetate and vinyl acetate copolymers, polyvinyl chloride and vinyl chloride copolymers, acrylate and methacrylate ester copolymers, polyethylene, polytetrafluoroethylene and other fluorinated polymers — have been developed over the past 40 years. Condensation polymers cannot be prepared by free-radical-initiated vinyl addition polymerization; therefore, latexes of these polymers — artificial latexes — are prepared by emulsification.

There are three methods to prepare latexes by emulsification: (i) direct emulsification, in which the polymer solution is emulsified in water to form an oil-in-water emulsion and the solvent is removed by distillation or extraction to form a dispersion of polymer particles; (ii) inverse emulsification, in which water is