APPLICATION OF PHASE-TRANSFER CATALYSIS TO THE REACTION OF ACRYLAMIDE WITH DIBUTYLAMINE IN WATER –HEPTANE SYSTEM

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ABSTRACT

The kinetics of the reaction between water soluble acrylamide and oil solyble dibutylamine in water-heptane bilayer system at high stirring rates and surface of the interface has been studied. The stirring rates results in the reaction rate's increase. The reaction occurs in the water phase at room temperatures.

Keywords: Michael's condensation, phase transfer catalysis, acrylamid, dibutilamine, water-heptane bilayer system.

INTRODUCTION

In organic synthesis very often arises necessity to carry out reactions between water soluble and oil soluble reagents. How to realize the reaction? Some principles have been worked out to solve this problem. One of them is to use water-organic solvents mixed solutions. Often as organic cosolvents aprotonic dipolar organic solvents, e.g. DMSO, DMF, are being used. But they are not always applicable because on one hand not in all cases they guarantee desired solubilites, on the other - they are expensive. The second principle had been worked out by Starks – Phase Transfer Catalysis (PTC) method [1]. The reaction was being carried out in oil - water bilayer system in the presence of a quaternary ammonium salt, which did not possess surfactant properties. The reaction occurred in the oil phase.

We applied the PTC methods to carry out Michael's type condensation.

The kinetics of the following reactions was studied: oil solyble butylacrylate + water soluble diethanolamin and water soluble N-[tri (hyroxymethyl)methane]acrylamide+oil solyble decylamine in water-heptane bilayer system was studied [2,3].

The aim of this work is to study the influence surface of the interface, the stirring speed on the reaction rate of water-soluble acrylamide (AA) with oil soluble dibutylamine (DBA) in the water-heptane two-phase system.

EXPERIMENTAL

AA and DBA (products of «Aldrich») were used without further purification, hexane (brand "spectroscopically pure") and distilled water were used. The reaction rate was determined by UV-spectroscopy method (spectrophotometer «Safas DES-170"). Optical density of AA aqueous solutions were determined at $\lambda = 220$ nm. Experiments were carried out in cylindrical glass reactors with different diameters. The volume ratio of the two phases was 1 : 1. Special magnetic stirrer with adjustable stirring rates was used.

RESULTS AND DISCUSSION

Spectroscopic studies showed that practically there was no AA in the heptane phase. Studies showed that the reaction rate at AA + DBA [DBA]> 1.0 M became independent of the concentration of DBA. The distribution of DBA in the water-heptane at T = 293 K showed that up to a concentration of [DBA] = 1.0 M the solubility of DBA in water increased to 0.15%, and remained constant.

It was shown that the initial rate of the reaction AA + DBA in water-heptane bilayer system was described by the equation:

$$R_r = k \, [AA]_0 \, [DBA]_0.$$

As it is seen from Table 1, with increase of separation surface between two phases (S) (coinciding with the cross section of the cylindrical reactor) the reaction rate increases symbatically.

Table 1.

Values of R_r and S at $[AA]_0=[DBA]_0=1,0$ M, T=293 K, $R_S = 100$ rpm.

S, sm^2	2	4	6	8	10
$10^5 R_r$, M $\bullet sec^{-1}$	2.1	3.0	4.2	5.3	6.4

As it is seen from Table 2, the stirring speed of the AA + DBA reaction symbatically increases with increase of the initial velocity due to increase of diffusion rate of DBA into the aqueous phase leading to an increase of the DBA concentration in water - reaction zone (reaction rate increases from $1.9 \cdot 10^{-5}$ M $\bullet sec^{-1}$ at $R_S =0$ rpm, to $4.0 \cdot 10^{-5}$ M $\bullet sec^{-1}$ at $R_S =1400$ rpm). The reaction proceeds at the water-heptane interface.

Table 2.

Effect of agitation rate on the reaction rate at $[AA]_0=[DBA]_0=1,0$ M, T=293 K, S = $2 sm^2$

R_S, rpm.	0	100	300	500	800	1000	1200	1400
$10^5 R_r$, M $\bullet sec^{-1}$	1.9	2.1	2.5	2.8	3.2	3.4	3.7	4.0

The general conclusion is the following: the PTC method may be successfully applied to carry out Michael's condensation in the bilayer water-oil system with using reagents one of which is water soluble and the other is oil soluble, with high rates at room temperatures.

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