REACTIONS OF DIPROPILAMINE WITY UNSATURATED SURFACTANTS IN THE MODEL OIL–WATER SYSTEM

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ABSTRACT

Kinetic of the reactions of dipropilamine with *N* [tris(hydroxymethyl)methyl]-acrylamide, in aqueous and organic solvents has been studied in the frame of the "oil–water" model. It has been shown that the reaction occurs in the micellar phase in aqueous medium. The reaction rate constant was well correlated with the solvent electrophilic parameter

Keywords*: oil, surfactant, amine, solvent, kinetics.*

INTRODUCTION

Petroleum products are among the most widespread and hazardous contaminants of surface waters. Oil is composed of more than 1000 organic compounds containing carbon, hydrogen, oxygen, sulfur, and nitrogen[1].

The nitrogen-containing petroleum products are generally divide into the nitrogen bases and neutral nitrogen compounds. The basic nitrogen compounds are majorly ternary amines, derivatives of pyridine, quinoline, isoquinoline, and acridine, the aniline derivatives being less common. Noteworthily, amines are not found exclusively in oil, they are formed in the hydrosphere via decomposition of proteins and phospholipids as well as due to direct deamination of amino acids [2]. Petroleum products form a number of various structures in aqueous phase, including the surface films, emulsions (oil-in-water or water-in-oil), petroleum aggregates, suspensions, or in the soluble forms absorbed with sediments and suspensions. The emulsion formation involves surface-active oil components: naphthene and carboxylic acids, resins, asphaltenes, etc [3]. The studies of petroleum products behavior in the hydrosphere has revealed that the oil decomposition is a multi-stage process consisting of a series of physical, chemical, and biological steps [4]. This work aimed to study the reactions of dipropilamine (DPA) with *N*[tris(hydroxymethyl)methyl]acrylamide (TA) in water and in organic solvents attempting their description in the frame of the "oil–water" model.

EXPERIMENTAL

TA and DPA (both from Aldrich) were used without further purification. Dimethylformamide DMF, dimethylsulfoxide DMSO, and formamide FA were purified as described in Ref. [5]. The rate of DPA reaction with the TA was measured at 293 K by means of US spectroscopy (Safas-170 instrument). The decay of TA concentration was monitored by measuring absorbance value at $\lambda = 230$ respectively.

RESULTS AND DISCUSSION

Variation of the initial concentration of the TA resulted in the variation of colloid properties of the reaction medium as well as in the change of the TA structure [6]. Therefore, the rate order and the rate constant of the reactions of TA with DPA were determined over wide ranges of the initial reactants concentration: $[TA]_0 = 1 \times 10^{-2}$–1.5 mol L^{-1}, and $[DPA]_0 = 1 \times 10^{-2}$–1.0 mol L^{-1}. The studied reaction obeyed the following rate equation:

$$W_0 = k\,[TA]_0[DPA]_0.$$

In contrast to the TA was soluble in DMF, DMSO, and FA. It was of interest to investigate the solvent effect on the TA + DPA reaction rate (Table 1). The reaction rate in various solvents followed the $H_2O > FA > DMSO > DMF$ series.

Similarly to the earlier studied case of surfaceinactive unsaturated compounds in the reaction with secondary amine [7], the TA + DPA reaction rate constant was well correlated with the solvent electrophilic parameter (E_T) [8]:

Table 1.

Rate constant of the TA + DPA reaction in aqueous and organic media at $T = 293$ K

Solvent	$10^4 k_{TA + DPA}$, mol^{-1}Ls^{-1}	E_T [8]
H_2O	16	63.1
FA	1.8	56.6
DMSO	0.15	45.0
DMF	0.12	43.8

$$\log k_{TA+DPA} = (-9.612 \pm 0.444) + (0.107 \pm 0.008)E_T,\ r = 0.99418.$$

To conclude, the studied reaction between the TA and DPA can serve as a simple model of certain processes occurring in natural hydrosphere systems containing oil. It was shown that the unsaturated compounds micellization reduced their reactivity as compared to that of the molecular forms.

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