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Reactions of Unsaturated Surfactants with Methylethanolamine in the Model Oil–Water System

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Abstract—Kinetic of the reactions of surface–active amides of unsaturated acids: *N*-[tris(hydroxymethyl)methyl]-acrylamide, sodium 4-acrylamidobutanoate, sodium 6-acrylamidohexanoate, and sodium 11-acrylamido-undecanoate with methylethanolamine in aqueous and organic solvents has been studied in the frame of the "oil–water" model. Changing of initial concentrations of the amides affects the colloid properties of the reaction medium as well as the amides reactivity. It has been shown that the reaction occurs in the micellar phase in aqueous medium.

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

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Petroleum products are among the most widespread and hazardous contaminants of surface waters. Oils and its processing products form extremely complex, labile, and diverse mixtures [1–3]. Oil is composed of more than 1000 organic compounds containing carbon (84–87%), hydrogen (12–14%), oxygen (0.005–3.6%), sulfur (1–2%), and nitrogen (usually below 1%) [1]. The nitrogen-containing petroleum products are generally divided 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. Alkylamines were not found in oil. Neutral petroleum nitrogen compounds are aryl derivatives of pyrrole, indole, carbazole, benzocarbazole as well as amides of saturated and unsaturated acids.

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 [4]. Phospholipids are esters of polyalcohols with one of the hydroxyl groups bound to a phosphorus acid instead of a carboxylic one; the phosphorus acid being in turn bound with a nitrogen base of an amino acid [5]. For example, some glycerophospholipids like phosphatidyl *N*-methylethanolamine form methylethanolamine MEA upon hydrolysis.

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 [2].

The stable and less reactive components of oil are included into the transformation via their deposition in the organic-inorganic complexes due to the similarities of oil components and certain biological matrices. We have earlier studied the influence of nature and concentration of the surfactant on the rate of the reaction between water-soluble diethanolamine and the hydrophobic butylacrylate in the two-phase water–heptane system [6, 7]. We have demonstrated the reaction acceleration in the presence of surfactant.

This work aimed to study the reactions between amides of unsaturated acids (AUA) with MEA in water and in organic solvents attempting their description in the frame of the "oil–water" model.

EXPERIMENTAL

N-[Tris(hydroxymethyl)methyl]acrylamide (TA) and *N*-methylethanolamine (MEA) (both from Aldrich) were used without further purification.

Table 1. Effect of the initial concentration of the AUA on the rate constant of their reaction with MEA at $T = 293$ K

$[AUA]_0$, mol L^{-1}	0.01	0.025	0.05	0.075	0.1	0.2	0.5	0.75	1.0
$k_{AB+MEA}\times10^5$, mol^{-1} L s^{-1}	55	55	55	53	52	51	51	51	51
$k_{AH+MEA}\times10^5$, mol^{-1} L s^{-1}	77	75	73	73	73	73	73	73	73

Table 2. Rate constant of the AUA + MEA reaction in water at $T = 293$ K and $[AUA]_0 >$ CMC along with the parameters determining the compounds reactivity

PAA	TA	AB	AH	AU
$k_{TA+MEA}\times10^4$, mol^{-1} L s^{-1}	33	5.1	7.3	6.0
E_T [11]	~1	0.12	0.046	0.0007
$q_{\beta C}$	+0.07	+0.054	+0.049	+0.058
q_{CO}	–0.361	–0.356	–0.386	–0.36

Sodium 4-acrylamidobutanoate (AB), sodium 6-acrylamidohexanoate (AH), and sodium 11-acrylamidoundecanoate (AU) were prepared, identified, and purified as described elsewhere [8]. Dimethylformamide DMF, dimethylsulfoxide DMSO, and formamide FA were purified as described in Ref. [9]. The rate of MEA reaction with the studied amides was measured at 293 K by means of US spectroscopy (Safas-170 instrument). The decay of TA, AB, AH, and AU concentration was monitored by measuring absorbance value at λ = 230, 215, 240, and 240 nm, respectively. Details of the procedure were earlier described in [6–8]. Quantum-chemical simulation of the amides molecules was performed taking advantage of the PM3 semiempirical method implemented in the HyperChem software package.

RESULTS AND DISCUSSION

Variation of the initial concentration of the AUA resulted in the variation of colloid properties of the reaction medium as well as in the change of the AUA structure [8]. Therefore, the rate order and the rate constant of the reactions of AUA with MEA were determined over wide ranges of the initial reactants concentration: $[TA]_0 = 1 \times 10^{-2}$–1.5 mol L^{-1}, $[AB]_0$ and $[AH]_0 = 1 \times 10^{-2}$–1.0 mol L^{-1}, $[AU]_0 = 10^{-2}$–10^{-1} mol L^{-1}, and $[MEA]_0 = 1 \times 10^{-2}$–1.0 mol L^{-1}.

The studied reaction obeyed the following rate equation:

$$W_0 = k\,[AUA]_0[MEA]_0.$$

In the case of TA, at $[TA]_0$ of 1×10^{-2} to 1.5 mol L^{-1} the reaction rate constant was independent of $[TA]_0$.

As the micelle forming ability of other AUA was higher than that of TA (Table 2), we has to study the effect of the reactants concentration on the reaction kinetics below and above the critical micellization concentration (CMC). As CMC was low in the case of AU, kinetic study was only possible at [AU] >> CMC.

Table 1 shows the rate constant of the AB + MEA and AH + MEA reactions at the AUA concentration below and above the CMC. The rate constant decreased with the $[AUA]_0$ increasing up to the CMC, and further remained independent of the AUA concentration (up to 1 mol L^{-1}).

The constant values of the reaction rate constant at [AUA] > CMC confirmed that the reaction involved the micelles of AB, AH, and AU.

The AUA reactivity could be confirmed using the kinetic data obtained at $[AUA]_0 >$ CMC, under conditions of the micelles formation (Table 2). From the results it followed that AB, AH, and AU containing hydrophobic fragments were less reactive towards MEA than TA containing three hydrophilic OH groups.

The reactivity of the studied amides with respect to MEA followed the TA > AB >AH > AU series.

Table 3. Rate constant of the TA + MEA reaction in aqueous and organic media at $T = 293$ K

Solvent	H_2O	FA	DMSO	DMF
$k_{TA+MEA}\times10^4$, mol^{-1} L s^{-1}	33.0	3.5	0.30	0.25
E_T [11]	63.1	56.6	45.00	43.80

Noteworthily, the series did not coincide with the amides CMC.

The data in Ref. [10] demonstrated that the rate of the reactions of selected unsaturated compounds (acrylonitrile, acrylamide, and methacrylamide) with secondary amines was correlated with the total charge at the β-carbon atom ($q_{\beta C}$).

Similarly to the case of the surface-inactive unsaturated compounds, reactivity of AUA (in addition to other factors) should depend on the total charge at the β-carbon atom. Such correlation between $\log k$ and $q_{\beta C}$ was revealed for the studied amides except for AH.

From the mechanism of the reaction between the unsaturated compounds and the secondary amine, the substrate reactivity should depend on both $q_{\beta C}$ and on the charge of oxygen atom of the CONH group (q_{CO}). Regarding the CMC as a measure of the AUA association ability, we proposed the empirical equation (1) relating the rate of the substrates reaction with MEA and the following parameters: $q_{\beta C}$, q_{CO}, and CMC.

$$\log k = a_0 + a_1 q_{\beta C} + a_2 q_{CO} + a_3 \mathrm{CMC}. \quad (1)$$

Even though the number of the substrates studied in this work was not sufficient to thoroughly analyze Eq. (1), we could estimate the importance of the proposed factors in determination of the reaction rate. In particular, the numeric values of the coefficients were as shown in Eq. (2).

$$\log k_{\mathrm{AUA+MEA}} = -6.955 + 19.625 q_{\beta C} - 7.204 q_{CO} + 0.456 \mathrm{CMC}. \quad (2)$$

Equation (2) revealed that the AUA reactivity towards MEA increased with the higher positive charge at the β-carbon, the higher (in terms of the absolute value) negative charge at the oxygen atom, and the higher CMC (i.e. decreasing the ability of the AUA towards association).

In contrast to the other studied AUA, TA was soluble in DMF, DMSO, and FA. It was of interest to investigate the solvent effect on the TA + MEA reaction rate (Table 3). The reaction rate in various solvents followed the H_2O > FA > DMSO > DMF series.

Similarly to the earlier studied case of surface-inactive unsaturated compounds in the reaction with secondary amine [12], the TA + MEA reaction rate constant was well correlated with the solvent electrophilic parameter (E_T) [11]:

$$\log k_{\mathrm{TA+MEA}} = (-10.256 + 0.502) + (0.106 + 0.010) E_T, \quad r = 0.99198.$$

To conclude, the studied reaction between the unsaturated amides and *N*-methylethanolamine 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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