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Kinetics of Reactions of α,β-Unsaturated Surfactants with Secondary Amines in a Solution

G. S. Simonyan*, N. M. Beileryan*, R. S. Arutyunyan*, J.-P. Roque, and A. Pavia****

** Erevan State University, Erevan, Armenia*

*** Montpelier-II University, France*

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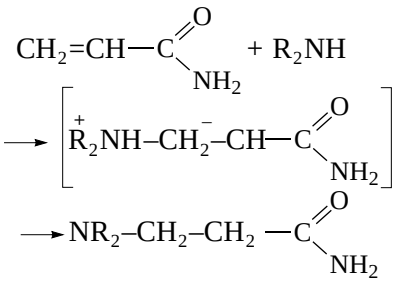
Abstract—The kinetics of reactions of acrylamide derivatives (acrylamidotrihydroxymethylmethane (TA), sodium 4-acrylamidobutanoate (AA_3), sodium 6-acrylamidohexanoate (AA_5), and sodium 11-acrylamidoundecanoate (AA10)) with piperidine and morpholine in water (for TA, also in DMF, DMSO, and formamide) is studied at 293 K. These compounds are weak surfactant monomers. The critical concentrations of micelle formation (CCM) for them are determined. The self-association of AA_3, AA_5, and AA_{10} producing micelles results in a decrease in their reactivity compared to the monomeric forms. The rates of the reactions of surfactant monomers (SM) with morpholine and piperidine are described by the second-order rate law $w_0 = k[SM]_0[Amine]_0$. An empirical equation is derived that relates the CCM values to the rate constant for the reaction of a surfactant monomer with a secondary amine with charges on the β-carbon and oxygen atoms of the amide group of a surfactant monomer. The rates of the reactions of TA with piperidine and morpholine are determined by the electrophilicity (acidity) of the medium, which is favorable for the Michael reaction.

INTRODUCTION

Finding the relationships between the colloidal and chemical properties of the reaction system and the reactivity of reactants provides insight into the kinetics and mechanism of a reaction. In the chemistry of monomers, including α,β-unsaturated compounds, many studies have been devoted to the synthesis of surfactant monomers (SMs) and various reactions in which they participate as reactants and agents forming media with molecular-level organization. According the basics of colloid chemistry of surfactant behavior of in water, the associates of monomeric molecules, micelles, are formed in solutions of surfactant monomers that are structurally similar to typical micelle-forming surfactants at their concentrations above the critical concentration of micelle formation (CCM). This can markedly change the rate of many chemical reactions [1, 2], specifically the polymerization of surfactant monomers [3].

The Michael addition of secondary amines to the double carbon–carbon bond is one of the reactions of α,β-unsaturated compounds. This reaction has been used as a model when developing the theory of nucleophilic addition.

The first stage includes the nucleophilic attack on the β-carbon atom of the double bond to yield an intermediate zwitter ion [4, 5]:



(I)

Then, this reaction is determined by the nature of reactants and a solvent. Note that the Michael reaction is a convenient model for studying the influence of the type of medium on the process rate.

In this work, we investigated how the structure of surfactant monomers and a solvent affect the kinetics of the reaction of surfactant monomers with secondary amines.

EXPERIMENTAL

The following compounds were used: piperidine (PP), morpholine (MP), and acrylamide derivatives, including acrylamidotrihydroxymethylmethane (TA), sodium 4-acrylamidobutanoate (**AA_3**), sodium 6-acrylamidohexanoate (**AA_5**), and sodium 11-acrylamidoundecanoate (**AA_{10}**).

Compounds AA_3, AA_5, and AA_{10} were synthesized according to the scheme

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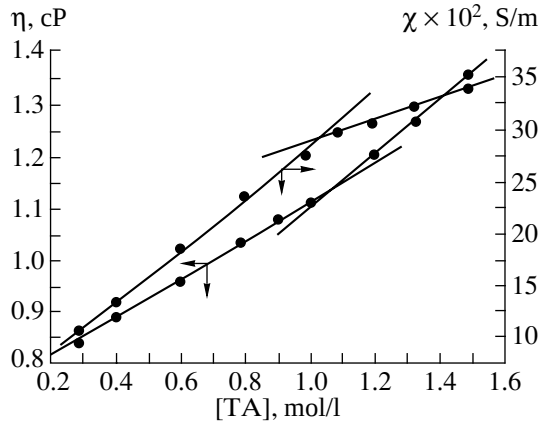


Fig. 1. Isotherms of the specific electric conductivity (χ) and viscosity (η) in water at T = 303 K.

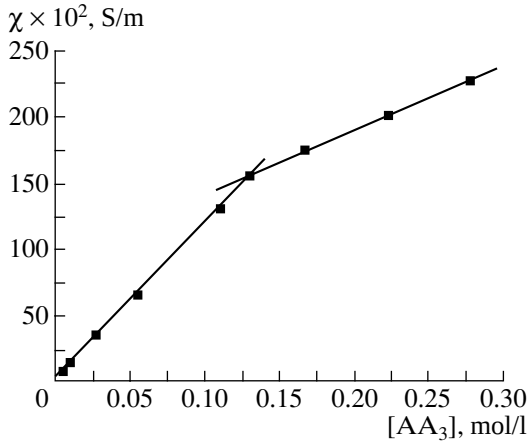
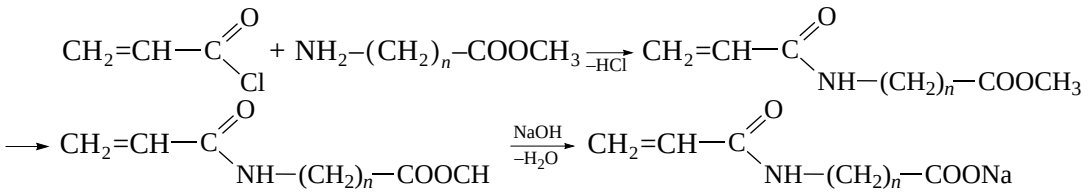


Fig. 2. Isotherm of the specific electric conductivity of AA_3 in water at T = 303 K.



n = 3 (AA_3), 5 (AA_5), 10 (AA_{10}).

The purity of AA_3, AA_5, and AA_{10} was determined by thin-layer chromatography. The concentration of the main substance in TA was 99.9%.

Surfactant monomers and the products of the reaction of TA with a secondary amine were identified by ^{1}H NMR spectroscopy with a Brucker ACG 250 instrument using D_2O as a solvent. Piperidine (PP), morpholine (MP), and the solvents (DMF, DMSO, and formamide) were purified as described in [6].

The rates of the reactions of surfactant monomers with secondary amines at 293 K were determined by spectrophotometry using a Safas-170 spectrometer. The consumption of TA, AA_3, AA_5, and AA_{10} was followed by a decrease in the extinction of aqueous solutions at λ = 230, 215, 240, and 240 nm, respectively. The procedure of determining a reaction rate is described in detail in [7]. The samples of DMF, DMSO, and formamide solutions were analyzed upon their dilution with water to prevent the effect of absorption of organic solvents. The error in determining the rate was at most 5%. The CCM values for the surfactant monomers were obtained from the isotherms of the surface tension (σ), by conductivity measurements, and by viscosity measurements for TA. The σ values of the aqueous solutions of surfactant monomers were measured by the method of the maximal pressure of a bubble using a Rebinder instrument [8]. The specific electric conductivity of solutions was determined as described in [9]. The relative errors in measuring the σ value and the specific electric conductivity was at most 2%.

The foam-forming ability was estimated from the foam stability (h) of 1% aqueous solutions of surfactant monomers determined from the ratio of the height of the foam column from 5 min after its formation to its initial height [10].

The surfactant monomer solutions were prepared by the weight method. The molar concentrations were calculated from the solution densities. Amines were added to the reaction medium by volume dilution.

RESULTS AND DISCUSSION

The results of colloid chemistry studies suggest that α,β-HC-unsaturated compounds are weak surfactants (Figs. 1–4). The colloid properties substantially depend on the number of methylene groups in the acrylamide molecules (n). The σ and CCM values decrease with an increase in the n parameter. The dependence of CCM on n for anion-active surfactant monomers (AA_3, AA_5, and AA_{10}) is expressed by the equation

$$\log \mathrm{CCM} = a + nb, \qquad (1)$$

which is typical of micelle-forming surfactants [8]. By solving Eq. (1), we obtain

$$\log \mathrm{CCM} = (0.269 \pm 0.127) - (0.342 \pm 0.082)n, \quad r = 0.994. \qquad (2)$$

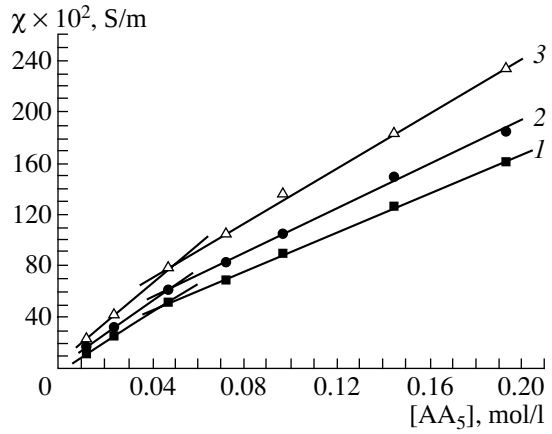


Fig. 3. Isotherms of the specific electric conductivity of AA_5 in water at T = (*1*) 303, (*2*) 313, and (*3*) 328 K.

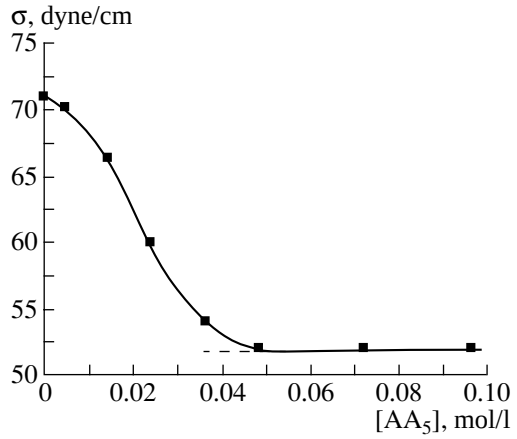


Fig. 4. Isotherm of the surface tension of AA_5 in water at T = 303 K.

The CCM values determined for TA by electric conductivity and viscosity measurements are nearly the same (Fig. 1). TA aggregates of different compositions (dimers, trimers, etc.) are formed in solutions. The CCM value for AA_5 is temperature independent (Fig. 3).

The surfactant monomers lack foam stability (h = 0), and this fact should be taken into account when studying kinetics in surfactant-containing systems.

The reactions of R_2NH with unsaturated compounds are bimolecular and described by the second-order rate laws [7, 11]. The available data on the reactions of secondary amines with surfactant monomers are lacking.

Variations in the initial concentrations of surfactant monomers cause changes in the colloidal properties of the reaction medium, as well as in their structure. Therefore, the reaction orders and the rate constants of the reactions of surfactant monomers with piperidine and morpholine were determined using data on the initial rate (w_0) over wide limits of the reactant concentrations:

$$w_0 = k[\mathrm{SM}]_0[\mathrm{Amine}]_0, \quad (3)$$

$$[\mathrm{TA}] = 10^{-2}\text{–}1.5 \text{ mol/l},$$

$$[\mathrm{AA_3}] \text{ and } [\mathrm{AA_5}] = 10^{-2}\text{–}1 \text{ mol/l},$$

$$[\mathrm{AA_{10}}] = 10^{-2}\text{–}10^{-1} \text{ mol/l},$$

$$[\text{Piperidine}] \text{ and } [\text{Morpholine}] = 10^{-2}\text{–}1 \text{ mol/l}.$$

Figure 5 presents some data obtained for the reaction of TA with piperidine.

To verify that reaction orders with respect to several compounds and the rate constants remain unchanged in the course of the reaction, we used the integral equation for the second-order reactions at $[\mathrm{SM}]_0 = [\mathrm{Amine}]_0$:

$$C^{-1} - C_0^{-1} = kt. \quad (4)$$

We found that the kinetic parameters fit Eq. (4) at $[\mathrm{TA}]_0 = [\text{Piperidine}]_0 = 10^{-1}$ mol/l (Fig. 6). The rate constants obtained by Eqs. (3) and (4) are almost the same and equal to k = 0.012 l mol^{-1} s^{-1}. Moreover, we also compared the conversion half-times $\tau_{1/2}$ for the pseudomonomolecular reaction of TA with piperidine at a great excess of amine: $[\text{Piperidine}]_0/[\mathrm{TA}]_0 = 10$. The $\tau_{1/2}$ value remains unchanged up to 75% conversion, which is typical of the first-order reactions. We found that $\tau_{1/2}$ = 10 min at $[\text{Piperidine}]_0$ = 0.1 mol/l, $[\mathrm{TA}]_0$ = 0.01 mol/l, and T = 293 K (Fig. 7). Then, $k[\text{Piperidine}]_0 = 0.695/\tau_{1/2} = 1.16 \times 10^{-3}$ s^{-1} and $k = 1.16 \times 10^{-2}$ l mol^{-1} s^{-1}, which almost coincide with the rate constants calculated by Eqs. (3) and (4).

The rate constants for the reactions of TA with piperidine and morpholine are independent of the $[\mathrm{TA}]_0$ value at TA concentrations ranging from 10^{-2} to 1.5 mol/l. Earlier [11], we established the same regularity when studying the reaction of acrylonitrile and acrylamide (AA) with piperidine in aqueous, DMF, DMSO, and formamide solutions. Note an inflection point observed on the electric conductivity and viscosity isotherms for the aqueous solutions of acrylamide at $[\text{Acrylamide}]_0$ = 0.9 mol/l. In this concentration range, the equilibrium is established between the acrylamide monomers and dimers, which exhibit almost the same reactivity in the reactions with piperidine and morpholine [12]. Obviously, this is also true of TA. The micelle-forming abilities of AA_3, AA_5, and AA_{10} are well above that of TA. This forced us to examine the effect of the concentrations of these surfactant monomers on the rates of the reactions with piperidine and morpholine at the [SM] values that were higher and lower than CCM. Taking into account that the CCM value is low for AA_{10}, the kinetic data for the reactions of AA_{10} with piperidine and morpholine were obtained only when $[\mathrm{AA_{10}}] \gg$ CCM.

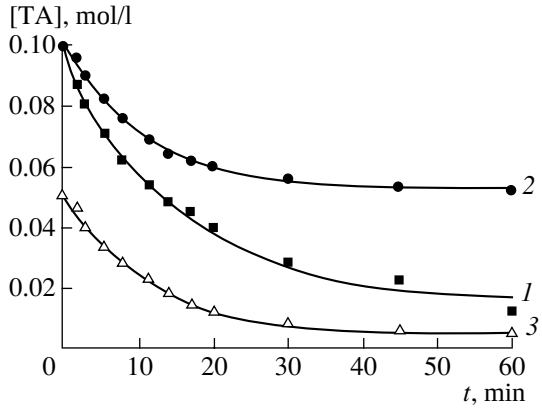


Fig. 5. Kinetic curves of TA consumption in water at (*1*) $[TA]_0 = [Piperidine]_0 = 0.1$ mol/l; (*2*) $[TA]_0 = 0.1$ mol/l and $[Piperidine]_0 = 0.05$ mol/l; (*3*) $[TA]_0 = 0.05$ mol/l and $[Piperidine]_0 = 0.1$ mol/l. $T = 293$ K.

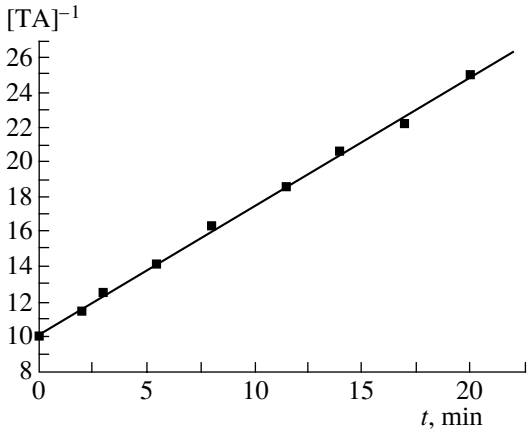


Fig. 6. $[TA]^{-1}$ as a function of the duration of the reaction of TA with piperidine in water at $T = 293$ K, $[TA]_0 = [Piperidine]_0 = 0.1$ mol/l.

The rate constants for the reaction of AA_3 and AA_5 with amines decrease with an increase in the surfactant monomer concentration up to a concentration equal to the CCM values and remain unchanged in more concentrated solutions (up to 1 mol/l). Below are the rate constants for the reaction of AA_3 with piperidine at the $[AA_3]$ values that are lower and higher than CCM:

$[AA_3]_0$, mol/l	0.01	0.05	0.075	0.1	0.2	0.5	0.75	1.0
$k \times 10^4$, l mol^{-1} s^{-1}	24	24	23	21	20	20	20	20

We obtained k values equal to 3.2×10^{-4}, 30×10^{-4}, and 4.2×10^{-4} l mol^{-1} s^{-1} for the reactions AA_3 + morpholine, AA_5 + piperidine, and AA_5 + morpholine, respectively, at surfactant monomer concentrations lower than the CCM value.

The fact that the reaction rate constants remained unchanged at $[SM]_0 > CCM$ (Table 1) suggests that the process involves the AA_3, AA_5, and AA_{10} micelles.

To compare the reactivates of surfactant monomers with respect to piperidine and morpholine, Table 1 presents the rate constants obtained for $[SM]_0 > CCM$, for which micelles are present in the reaction medium. Compounds AA_3, AA_5, and AA_{10} containing hydrophobic groups exhibit a lower reactivity than TA with three hydrophilic OH groups.

According to their reactivity in the reactions with piperidine and morpholine, the surfactant monomers studied may be arranged in the following series: TA > AA_5 > AA_{10} > AA_3. However, this series does not correlate with the corresponding CCM values.

Table 1. The rate constants for the reaction of surfactant monomers with piperidine and morpholine in water and parameters determining their reactivity (Eq. (6))

Parameter	Surfactant monomer			
	TA	AA_3	AA_5	AA_{10}
$k^{293}_{SM+PP} \times 10^4$, l mol^{-1} s^{-1}	120	20	26	24
$k^{293}_{SM+MP} \times 10^4$, l mol^{-1} s^{-1}	15	2.8	3.5	3.0
σ*, dyne/cm	–	61	52	44
CCM, mol/l	~1	0.12	0.046	0.0007
$q_{\beta\text{-C}}$	+0.07	+0.054	+0.049	+0.058
q_{CO}	−0.361	−0.356	−0.386	−0.36

* At [SM] = CCM, 303 K.

Earlier, several researchers attempted to establish a quantitative correlation between the structure and reactivity of unsaturated compounds in their reactions with nucleophilic species. For example, correlations were obtained between the logarithms of the rate constant and the *e*/*Q* ratios (*e* and *Q* are the Alfrey and Price parameters, respectively [13]) for the reactions of secondary amine with unsaturated compounds (acrylonitrile, methacrylate, methyl methacrylate, etc.) in DMF [5] and reactions of secondary amines with unsaturated compounds (acrylamide, methacrylamide, etc.) in water [7]. This correlation was considered in detail in [5]. The *e* and *Q* parameters for surfactant monomers are unknown.

Along with other factors, the reactivity of unsaturated compounds (see scheme I) should depend on the overall charge on the β-carbon atom ($q_{\beta\text{-C}}$). The quantum-chemical calculations of surfactant monomers, acrylonitrile, acrylamide, and methacrylate were performed using HyperChem and the semiempirical PM3 method.

For acrylonitrile, acrylamide, and methacrylamide, correlations were obtained between the $q_{\beta\text{-C}}$ and *e*/*Q* parameters

$$q_{\beta\text{-C}} = (0.0116 \pm 0.0052) + (0.034 \pm 0.0031)e/Q, \quad r = 0.994 \tag{5}$$

and, consequently, between the rate constants for the reactions of these unsaturated compounds with secondary amines and the $q_{\beta\text{-C}}$ charge. The $\log k$ vs. $q_{\beta\text{-C}}$ correlation is also true for the surfactant monomers studied, except for AA_5.

In our opinion, one should also consider the charge at the oxygen atom of the CONH fragment (q_{CO}) along with the $q_{\beta\text{-C}}$ parameter. We took the CCM parameter as a measure of the association of surfactant monomers and derived an empirical equation relating the logarithm of the rate constant of the reaction between the surfactant monomer and amine to parameters $q_{\beta\text{-C}}$, q_{CO}, and CCM for surfactant monomers:

$$\log k = a_0 + a_1 q_{\beta\text{-C}} + a_2 q_{CO} + a_3 \text{CCM}. \tag{6}$$

Although the number of surfactant monomers is insufficient for solving Eq. (6) correctly (the estimation of the correlation coefficient, the root-mean-square deviation, etc.), this equation still allows the assessment of the contribution of the $q_{\beta\text{-C}}$, q_{CO}, and CCM parameters to the rate constant for the reaction between the surfactant monomer and the secondary amine. By solving Eq. (6) for the reactions of a surfactant monomer with piperidine and morpholine, we obtain

$$\log k_{\text{CM + PP}} = -6.945 + 23.729 q_{\beta\text{-C}} - 8.190 q_{CO} + 0.406\text{CCM}, \tag{7}$$

$$\log k_{\text{CM + MP}} = -6.966 + 15.512 q_{\beta\text{-C}} - 7.064 q_{CO} + 0.506\text{CCM}. \tag{8}$$

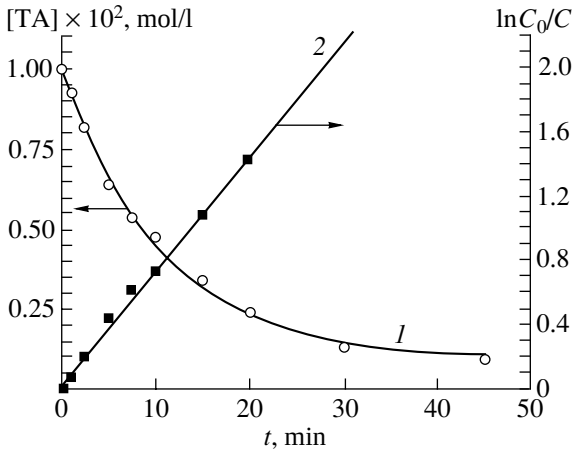


Fig. 7. Kinetic curve of TA consumption in water (*1*) and its semilogarithm anomorphosis (*2*). T = 293 K, $[TA]_0$ = 0.01 mol/l, and $[Piperidine]_0$ = 0.1 mol/l.

It follows from Eqs. (7) and (8) that the higher the positive charge on the β-carbon atom and the lower the negative charge on the oxygen atom, the more active a surfactant monomer in its reaction with piperidine and morpholine. An increase in the CCM value, which is a decrease in the association ability of a surfactant monomer, causes an increase in the rate constant for the reaction of a surfactant monomer with the secondary amine.

Taking into account that TA is soluble in DMF, DMSO, and formamide (whereas the other surfactant monomers are insoluble in these solvents), we studied the influence of solvents on the rates of the reaction of TA with piperidine and morpholine (Table 2).

The rate constants for the reaction of TA with a secondary amine in the solvents studied may be arranged in the series: H_2O > formamide > DMSO > DMF. The same series was observed earlier for the reaction of acrylonitrile with morpholine [7]. This series does not correlate with the dielectric permeability of the medium ε (formamide does not fit this series).

As for the reaction of acetonitrile with morpholine [7], we obtained a good correlation between $\log k$ for the reactions of TA with piperidine and morpholine and the Dimroth–Reichardt electrophilicity of solvents E_T [15]:

$$\log k_{\text{TA + PP}} = (-8.496 \pm 0.361) + (0.103 \pm 0.007)E_T, \quad r = 0.996, \tag{9}$$

$$\log k_{\text{TA + MP}} = (-10.135 \pm 0.405) + (0.114 \pm 0.008)E_T, \quad r = 0.995. \tag{10}$$

Based on the kinetic data given in [16], we also established a correlation between the $\log k$ and E_T values for the reaction of methyl acrylate with ethanola-

Table 2. The effect of solvents on the rate constant for the reaction of TA with piperidine and morpholine at 293 K

Solvent	H_2O	Formamide	DMSO	DMF
$k_{TA+PP} \times 10^4$, l mol^{-1} s^{-1}	120	13	1.4	1.1
$k_{TA+MP} \times 10^4$, l mol^{-1} s^{-1}	15	1.6	0.1	0.085
ε_{293} [14]	80.1	111.5	48.9	36.7
E_T [15]	63.1	56.6	45.0	43.8

mine in 1,4-dioxane, piperidine, DMF, acetonitrile, and CH_3OH used as solvents:

$$\log k = -1.997 + 0.0088E_T, \quad r = 1. \qquad (11)$$

Correlations (9)–(11) for the reaction of an unsaturated compound with amine suggest that the main parameter of solvents that determines the effect of a medium on the rate constant for the reaction of a surfactant monomer with R_2NH is its electrophilicity E_T, which characterizes the ability of a solvent to both nonspecific and specific solvation.

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