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Basicity of amides in water and in aqueous micellar solutions of SDS

Their influence on micellar structure

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The acidity constants of the protonated forms of some amides, including formamide, *N*-methylformamide, *N*,*N*-dimethylformamide, *N*-methylacetamide and *N*,*N*-dimethylacetamide, have been determined in water and in aqueous micellar solutions of sodium dodecyl sulfate (SDS). The influence of these amides on the acid hydrolysis of 1-phenylethylnitrite was studied by UV absorption spectroscopy. The observed inhibition, in water as well as in an aqueous micellar medium, in the reaction rate by the presence of amides has been quantitatively interpreted by considering the action of amides as weak bases. Solvent effects at high amide concentrations were also considered. The experimental kinetic data obtained in the presence of SDS were analysed using the simple pseudophase ion-exchange model and taking into account the effects of amides on the structure of micelles.

In recent years, compartmentalized liquids have found potential uses and applications in various fields related to chemistry and biology.[1,2] Micelles and other association colloids act as 'microreactors', compartmentalizing and concentrating, or separating and diluting reactants and thereby altering the apparent rate and equilibrium constants of chemical reactions.[3–5]. The properties of micellar solutions, such as critical micelle concentration (c.m.c.), aggregation number (*N*), and micelle size and shape, depend on the balance between 'hydrophobic' and 'hydrophilic' interactions. In aqueous solutions of ionic surfactants this balance may be modified by (*a*) salt addition, (*b*) counterion complexation, (*c*) addition of substances that can be solubilized into the micelle or (*d*) changing the solvent or the 'structure' of the solvent itself by adding non-electrolytes, *i.e.* ureas. The influence of the addition of salts and polar molecules, such as ureas[6] and alcohols,[7] on the properties of aqueous surfactant solutions has been thoroughly studied.

In a previous paper we studied the influence of urea and alkyl ureas on the properties of aqueous micellar solutions of SDS.[8] We performed conductivity measurements and carried out a kinetic study of the acid hydrolysis of 1-phenylethylnitrite (PEN) to investigate the effect of ureas. The observed inhibition, in water as well as in aqueous micellar solutions of SDS, has been quantitatively explained by viewing the action of ureas as weak bases, which protonate themselves and thus reduce the effective H^+ concentration. The degree of protonation was increased in the presence of SDS micelles as a result of the association of the protonated urea with the negatively charged micellar surface. In the case of tetramethylurea a medium effect was also observed, because this urea decreases the relative permittivity of the water mixtures.

Here we have studied the influence of some amides, including formamide (FMD), methylformamide (MFD), dimethylformamide (DMF), *N*-methylacetamide (MAC) and *N*,*N*-dimethylacetamide (DMAC). These compounds, except DMF and DMAC,[9] possess high and similar dipole moments and a relative permittivity higher than that of water. The results provide a way of determining the basicity constants of amides in water without using drastic conditions but in conjunction with a precise method. The acidity constants of protonated amides have been measured using several methods. Nevertheless, literature values of the pK_a of protonated amides vary widely, partly owing to the drastic conditions used, which reflects the well known difficulty of measuring the acidity constants of moderately strong acids.[10–13]

Experimental

FMD and DMF (Merck p.a. products) and MFD, MAC and DMAC, (Aldrich p.a. products) were purified by fractional distillation. (The pH of a 0.50 mol dm^{-3} aqueous solution of DMF was 6.85 which agrees perfectly with that reported by Merck Index; the pH of a 2 mol dm^{-3} aqueous solution of MFD was 6.40. These pH values indicate the lack of amines as impurities.) Pyrene (Aldrich) was purified by column flash chromatography using silica gel as stationary phase and cyclohexane as eluent. 1-Phenylethylnitrite was synthesized by treating 1-phenylethanol with sodium nitrite in aqueous sulfuric acid, purified by fractional distillation, and stored at low temperatures over molecular sieves (3 Å) to prevent hydrolysis.[14] All other reagents (Merck or Aldrich) were of the maximum purity commercially available and were used as received.

Specific conductivities were measured in a Knick microprocessor conductimeter provided with a four-pole measuring cell with temperature sensor, using solutions prepared with doubly distilled water. The calibration of the conductimeter was carried out by measuring the conductance of dilute KCl solutions at 25 °C. The measured cell factor was 1.10 cm^{-1}. The solutions were thermostated in a conductivity cell equipped with a magnetic stirring device.

Steady-state fluorescence spectra were recorded on an Aminco–Bowman spectrofluorimeter at 25 °C. Pyrene was excited at 334 nm (absorbance <0.1) and its emission was recorded at 373 and 384 nm, corresponding to the first and third vibronic peaks, and with the use of excitation and emission slits of 8 and 1 nm, respectively.

The reaction rates were studied by using a Hi-Tech stopped-flow apparatus, noting the decreasing absorbance due to the consumption of alkyl nitrite at 260 nm. The kinetic procedure has been described elsewhere.[8] Each reported k_0 value is the average of at least four individual measurements with a typical variation of ±1% or less (variations higher than 0.4 absorbance units were monitored).

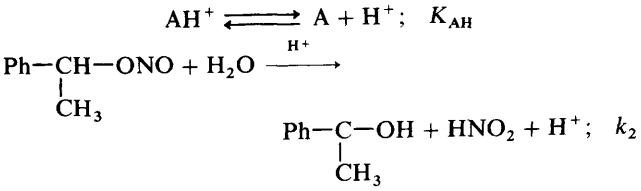
Results and Discussion

Effect of amides in water

Kinetic measurements. The acid hydrolysis of PEN in an aqueous medium has been studied previously.[14] The reaction goes through a concerted mechanism that involves both proton transfer and the breaking of the N—O bond through an asymmetric transition state. Fig. 1 shows the influence of acidity in water in the absence and presence of 1.0 mol dm^{-3} of DMF and of MAC. In every case the influence of acidity (controlled with HCl) leads to the linear relationship:

$$k_0 = k_1[\mathrm{H}^+] \qquad (1)$$

Analysis of the influence of amide concentration at constant [H$^+$] shows that the reaction is inhibited by the addition of amide. Typical data obtained in the cases of DMF and FMD are displayed in Fig. 2. This inhibition effect can be explained, as in the case of ureas,[8] if one considers the basic character of amides, and this is represented in Scheme 1.



$$\mathrm{AH^+ \rightleftharpoons A + H^+};\quad K_{\mathrm{AH}}$$

$$\mathrm{Ph{-}\underset{\displaystyle CH_3}{\underset{|}{C}}H{-}ONO + H_2O \xrightarrow{H^+} Ph{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}OH + HNO_2 + H^+};\quad k_2$$

Scheme 1

where AH$^+$ represents the protonated form of the amide, A, the unprotonated form and K_{AH}, the acid ionization constant of AH$^+$. From Scheme 1 and taking into account that $[\mathrm{H}^+]_t = [\mathrm{H}^+] + [\mathrm{AH}^+]$ and $[\mathrm{A}]_t = [\mathrm{A}]$ (since in every case $[\mathrm{A}] > 10[\mathrm{H}^+]$), one may obtain the following expression for the observed rate constant, k_0:

$$k_0 = \frac{k_2 K_{\mathrm{AH}}[\mathrm{H}^+]_t}{K_{\mathrm{AH}} + [\mathrm{A}]} \qquad (2)$$

Eqn. (2) predicts a linear dependence of k_0 on $[\mathrm{H}^+]_t$ in the absence of amide or at constant amide concentration, as was found experimentally, and decreasing k_0 as [amide] increases at constant [H$^+$]. The data can be linearized in the form $1/k_0$ *vs.* [amide]. As may be seen from the data in Fig. 2, this is the generally observed behaviour at amide concentrations of less than *ca.* 1.5 mol dm^{-3}. At higher [amide] levels, k_0 decreases more quickly than eqn. (2) predicts because of solvent effects. One can also observe that the inhibition effect is more pronounced with the more polar amides; *e.g.* the observed rate constant k_0, in the absence of amide is 14 times as high as that in the presence of 4 mol dm^{-3} of FMD (the relative permittivity of FMD is 111 at 20 °C),[9] meanwhile, it is only six times as high as that determined in the presence of the same concentration of DMF, which has a relative permittivity around 36. However, when the solvent effects are not important, *i.e.* at [amide] $\leqslant$ 1 mol dm^{-3}, the inhibition effect is higher for the most basic amide, DMAC in this case (see below).

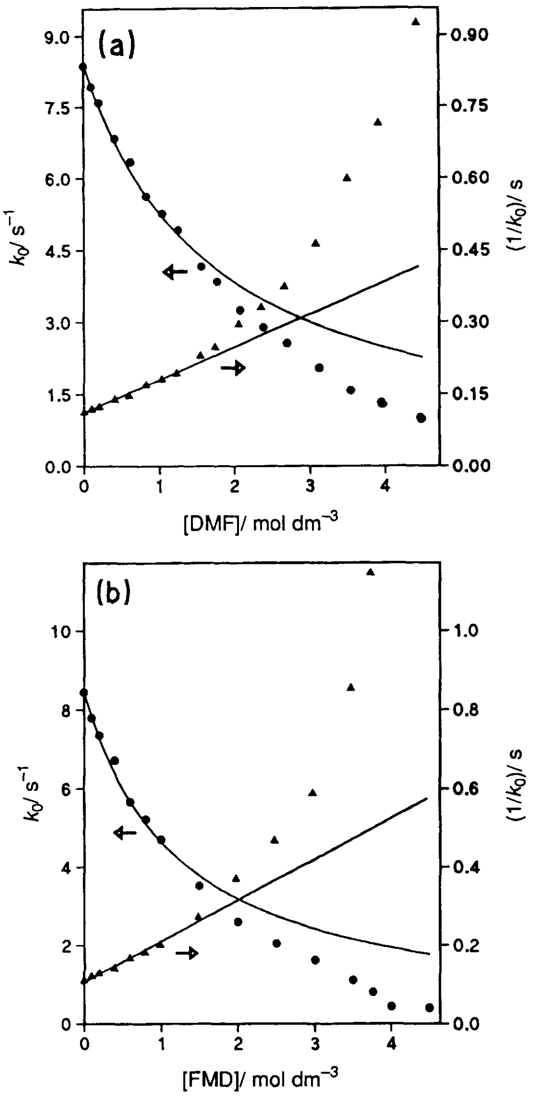


Fig. 2 Influence of (●) DMF (a) and FMD (b) on the pseudo-first-order rate constant of the hydrolysis of PEN in water at [HCl] = 1.27 × 10^{-2} mol dm^{-3} and (▲) linearization of the data according to eqn. (2)

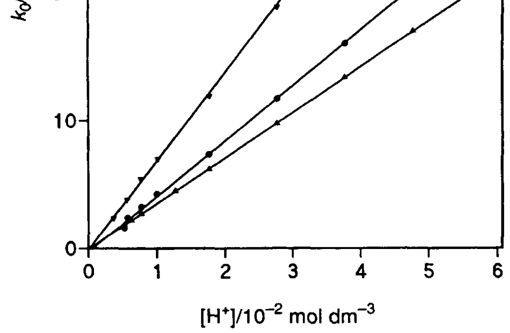
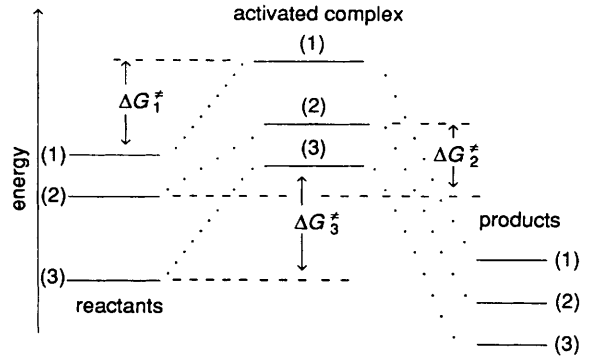


Fig. 1 Influence of acidity (HCl) on the pseudo-first-order rate constant for the acid hydrolysis of PEN in water at (▼) no added amides, (●) [DMF] = 1.0 mol dm^{-3} and (▲) [MAC] = 1.0 mol dm^{-3}

The acid hydrolysis of PEN shows significant medium effects. The addition of DMF and DMAC (non-hydrogen-bonding solvents) to water decreases the relative permittivity of the corresponding mixtures, while FMD, MFD and MAC (hydrogen-bonding solvents) increase the relative permittivity of water mixtures. Both effects are reflected in the kinetic results obtained at [amide] $\geqslant$ 1.5 mol dm^{-3}. Under these experimental conditions, two factors cause k_0 to decrease as [amide] increases: the reduction of the effective [H$^+$] and the solvent effects. In line with Reichardt's treatment for solvent effects on the rate of reactions,[15] the effect of amides can be understood by taking into account the solvation of the different species. The initial reactants [H^+ and $PhCH(CH_3)O{-}NO$], as well as the activated complex are solvated, but to a different extent. The solvation of the products obviously does not have any influence on the reaction rate. The less polar amides (DMF and DMAC, as well as alkylureas[8]) decrease the polarity of aqueous mixtures. The resulting less-polar solvent stabilizes the activated complex (the alkoxide being the leaving group) more than it destabilizes the reactants: the reaction is slowed down by the solvent.

On the other hand, since the charge is more localized on the reactant H^+ than on the activated complex, the former will be better solvated than the latter. This differential solvation of reactants and activated complex is greater for protic solvents, *i.e.* HBD solvents such as FMD, MFD or MAC, which produce aqueous solutions of higher polarity; in such a case, a strong stabilization of the reactants and a destabilization of the activated complex occur, resulting in a greater decrease in reactant enthalpy compared to that of the activated complex. Scheme 2 illustrates the situation:



Scheme 2 One-dimensional Gibbs energy diagram for the reaction in (1) aqueous solutions of the less polar amides, (2) water and (3) aqueous solutions of the more polar amides

Table 1 lists the values of k_1 obtained from studying the influence of acidity under the various experimental conditions and those calculated from the values of k_2 and K_{AH}. Both parameters were determined by studying the influence of amide concentration in the range $0 < [\text{amide}]/\text{mol dm}^{-3} \leqslant 1.3$, and are also reported in Table 1. Earlier data on protonated amide pK_{AH} values are also shown. Spectroscopic (UV-VIS absorption and NMR), potentiometric and conductimetric methods have been used[10–13] to determine the relative concentrations of A and AH^+ in a concentrated acid solution. The wide spread of K_{AH} values reported reflects both the difficulty in measuring these particular concentrations spectroscopically and the uncertainties in the techniques for extrapolation to infinite dilution. We believe that the indirect method described here is clearly superior, thus we used (i) a UV absorption method at an accurate wavelength; (ii) a hydrolysis reaction very sensitive to [H^+] whose mechanism is the direct reaction and (iii) neither drastic [acid] conditions nor extrapolation of the results, both being unnecessary.

Effect of amides in SDS micellar solutions

Critical micelle concentration. The c.m.c. of SDS, determined conductimetrically at 25 °C (see Fig. 3), shows a slight increase with increasing [amide] (see Table 2). Its value in water, 8.0×10^{-3} mol dm^{-3} agrees with that in the literature.[16] The c.m.c. values determined kinetically in the presence of 0.013 mol dm^{-3} of HCl are also listed in Table 2. Obviously, these values are lower than those determined by

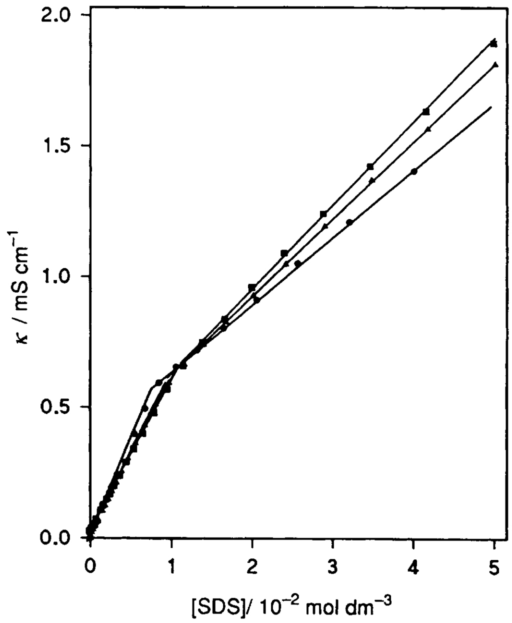


Fig. 3 Specific conductivities of SDS aqueous solutions at (●) no added amides; (▲) [MAC] = 0.50 mol dm^{-3} and (■) [MAC] = 1.0 mol dm^{-3}

Table 1 Pseudo-second order rate constants (k_1), bimolecular rate constants (k_2) and the acid ionization constants (K_{AH}) of the protonated form of amides obtained in aqueous hydrochloric acid medium ([HCl] = 1.27×10^{-2} mol dm^{-3}) from the kinetic study of the hydrolysis of PEN

amide	ε^a	$k_1{}^b$	$k_2{}^b$	$K_{AH}{}^c$	$K_{AH}{}^d$	method	ref.
FMD[e]	111	390 ± 8	707	1.23	0.76,[f] 1.78[g]	UV spectra	10
FMD[h]	111	371[i]	672 ± 10	1.23 ± 0.07	3.02	potentiometric	11
MFD[e]	182.4	490 ± 7	694	2.4	0.30;[f] 0.71[g]	VIS spectra	10
MFD[h]	182.4	464[i]	657 ± 8	2.4 ± 0.1	1.10	potentiometric	11
DMF[e]	36.7	432 ± 4	685	1.71	0.66,[f] 1.55[g]	VIS spectra	10
DMF[h]	36.7	422[i]	668 ± 7	1.71 ± 0.07	1.02	potentiometric	11
					15.8	conductance	12
MAC[e]	191.3	355 ± 1	675	1.11	0.55,[f] 1.29[g]	VIS spectra	10
MAC[h]	191.3	346[i]	657 ± 12	1.11 ± 0.08	0.16	potentiometric	11
					2.63	conductance	12
					2.88	UV spectra	13
DMAC[e]	37.8	263 ± 1	668	0.65	0.24,[f] 0.56[g]	VIS spectra	10
DMAC[h]	37.8	264[i]	670 ± 9	0.65 ± 0.03	1.90	conductance	12
					1.55	UV spectra	13

[a] Relative permittivity for the pure liquid at 25 °C, except FMD, 20 °C and MAC, 32 °C, taken from ref. 9; [b] in mol^{-1} dm^3 s^{-1}; [c] this work; [d] literature values; [e] from the influence of acidity, eqn. (1) at [amide] = 1.0 mol dm^{-3}; [f] at $I = 0.55$; [g] thermodynamical value; [h] from the influence of [amide], eqn. (2) at [H^+] = 0.0127 mol dm^{-3}; [i] estimated from k_2 and K_{AH} at [amide] = 1.0 mol dm^{-3}.

Table 2 Values of c.m.c., aggregation numbers (N) and the fractional micellar charge neutralized (β) of SDS micelles determined in the presence of amides

amide[a]	10^3 c.m.c.[b]	slope[c]	N[d]	S_1[e]	S_2[e]	β[f]
—	3.5,[g] 8.0[h]	3244 ± 60	55	73.7 ± 0.2	25.6 ± 0.1	0.79 (0.65)
FMD (0.5)	3.6,[g] 8.2[h]	—	67	68.7 ± 0.2	27.3 ± 0.06	0.77 (0.60)
FMD (1.0)	4.2,[g] 8.7[h]	1444 ± 36	66	66.7 ± 0.2	28.6 ± 0.1	0.75 (0.57)
MFD (0.5)	3.6,[g] 8.5[h]	—	62	66.0 ± 0.1	29.0 ± 0.1	0.75 (0.56)
MFD (1.0)	4.5,[g] 8.2[h]	1332 ± 49	61	62.8 ± 0.2	31.6 ± 0.1	0.71 (0.48)
DMF (0.5)	3.8,[g] 8.7[h]	1308 ± 32	60	64.7 ± 0.1	30.7 ± 0.1	0.71 (0.53)
DMF (1.0)	4.5,[g] 10.1[h]	965 ± 59	44	58.8 ± 0.2	32.4 ± 0.2	0.71 (0.45)
MAC (0.5)	3.5,[g] 9.6[h]	1293 ± 42	60	63.2 ± 0.1	29.7 ± 0.2	0.72 (0.53)
		1292 ± 5[h]	52	—	—	—
MAC (1.0)	3.8,[g] 11.5[h]	1202 ± 50	55	57.0 ± 0.2	31.8 ± 0.3	0.63 (0.44)
	4.3[i]	1159 ± 16[h]	45	—	—	—

[a] Values in parentheses are [amide] in mol dm^{-3}; [b] in mol dm^{-3}; [c] the slopes of the plots $\ln(I_0/I)$ vs. [CPyC], see eqn (3); [d] at [SDS] = 0.05 mol dm^{-3}; [e] in Ω^{-1} equiv^{-1} cm^2; [f] β values determined from eqn. (4) and from the method of slopes (values in parentheses); [g] kinetic value at [HCl] = 0.0127 mol dm^{-3}; [h] no HCl; [i] from fluorescence measurements.

electrical conductivity, owing to depression of the c.m.c. by the presence of electrolytes,[17] which decrease the thickness of the ionic atmosphere surrounding the ionic head groups and the consequent decreased electrical repulsion between them in the micelle. There is a satisfactory agreement between the 'kinetic' c.m.c. values and those determined from fluorescence measurements of pyrene. Pyrene is a strongly hydrophobic probe with very low solubility in water. The fluorescence spectrum of pyrene at a low concentration (2×10^{-6} mol dm^{-3}) in homogeneous solutions possesses a considerable fine structure whose relative peak intensities undergo significant perturbation upon going from polar to non-polar solvents.[18] The variation of $I_{\mathrm{I}}/I_{\mathrm{III}}$ (fluorescence intensities of the first and third vibronic peaks) measured as a function of SDS concentration shows an abrupt change when micelles are formed [see Fig. 4(a)] since pyrene is poorly soluble in water and is preferentially solubilized in the interior hydrophobic region of the micelle.

Amides are among the additives that change the c.m.c. of surfactants by modifying solvent–micelle or solvent–surfactant interactions. Therefore, to be effective, the bulk-phase concentrations of these additives are usually high, but the effect is small, as it is shown in the results in Table 2.

Aggregation numbers. Following Turro and Yekta,[19] the aggregation numbers of SDS in the presence of amides were estimated from changes in the fluorescence intensity of pyrene through the addition of cetylpyridinium cloride (CPyC) at (0.4–4) × 10^{-4} mol dm^{-3}. All measurements were carried out at 25 °C and 0.050 mol dm^{-3} of SDS with 2.8×10^{-6} mol dm^{-3} of pyrene at amide concentrations of 0.50 and 1.0 mol dm^{-3} and in the presence of [HCl] = 0.015 mol dm^{-3}. This technique assumes that the number of both probe and quencher molecules per micelle have Poisson distributions.[20] In the case of an inmobile and static quencher,[21] the ratio of fluorescence intensities in the absence (I_0) and in the presence (I) of quencher is given by eqn. (3), and the mean surfactant aggregation number (N) is obtained from the slope of the plot of $\ln(I)$ vs. [CPyC], where Fig. 4(b) is an example.

$$\ln(I_0/I) = \frac{N[\mathrm{CPyC}]}{[\mathrm{SDS}] - \mathrm{c.m.c.}} \qquad (3)$$

The values of N reported in Table 2 correspond to the c.m.c. values ('kinetic' c.m.c. values).

Fractional micellar ionization. Conductivity measurements were performed in the absence and presence of amides. The determination of α was based on either of two general methods. The simplest is the 'method of slopes', in which α is the ratio of the slopes of plots of conductance vs. [surfactant] above and below the c.m.c.[22] This method assumes that the contribution of the micelle to the conductance is the same as that of an equivalent number of monomeric ions, the sum of whose charges equals the micelle charge. This assumption is least satisfactory when α is high, and values of α calculated

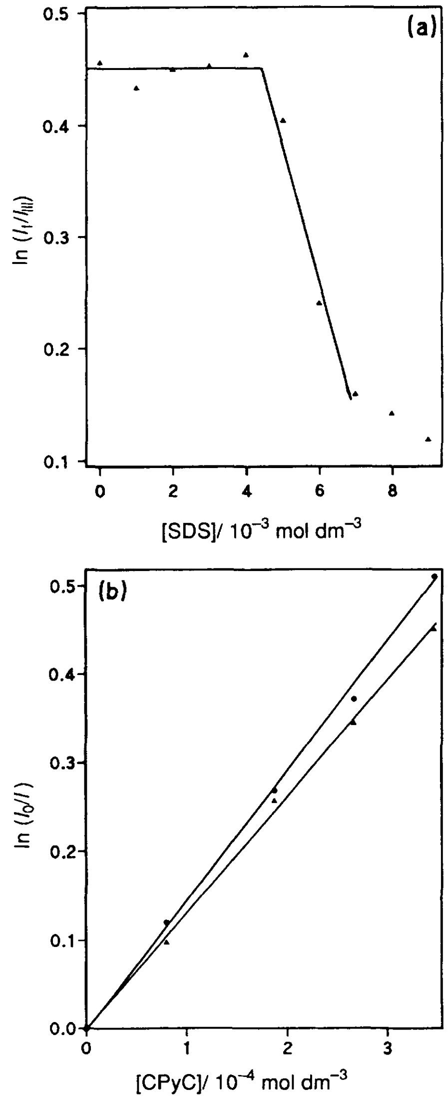


Fig. 4 (a) Ratio of fluorescence intensities of the first and third vibronic peaks of pyrene as a function of [SDS] at [HCl] = 0.013 mol dm^{-3} and (b) ratio of luminescence intensities of pyrene in the absence and presence of quencher as a function of the CPyC concentration, in aqueous solutions of 0.050 mol dm^{-3} SDS at [H$^+$] = 0.013 mol dm^{-3} and (●) [FMD] = 1.0 mol dm^{-3} and (▲) [DMF] = 0.50 mol dm^{-3}

using this method are higher than those calculated in terms of the micellar contribution to conductance, estimated by using Evans' equation.[23] The relation between conductance and [surfactant] is given by eqn. (4):

$$1000S_2 = \frac{(N-m)^2}{N^{4/3}}(1000S_1 - \Lambda_{\mathrm{Na}}) + \frac{(N-m)}{N}\Lambda_{\mathrm{Na}} \qquad (4)$$

where S_1 and S_2 are slopes of plots of specific conductance (in S cm^{-1}) *vs.* [surfactant] below and above the c.m.c., respectively, and where Λ_{Na} is the equivalent conductance of counterion, Na$^+$, and taken as 50.11 cm^2 equiv^{-1} Ω^{-1} from ref. 24. Eqn. (4) is solved for *m*, the number of bound counterions, so that $m/N = 1 - \alpha\ (=\beta)$. Values of β determined using the two methods are given in Table 2. As one may see, there are large differences between conductometric values of β determined by the use of Evans' equation and the method of slopes. We have used Evans' equation values of β to fit kinetic data (see below) in order to obtain the best fits.

Kinetic measurements. The influence of SDS and amide concentrations on the hydrolysis of PEN was studied at fixed HCl concentration ($=1.27\ 10^{-2}$ mol dm^{-3}). Fig. 5 shows typical results of the effects of SDS and DMF concentrations. Fig. 6 shows the comparative effect found with the amides used in the present work.

The observed rate constant increases with SDS concentration, goes through a maximum, and decreases at still higher concentrations of SDS. The catalytic effect, *i.e.* the maximum value of k_0 obtained, decreases as [amide] increases, and the effect is more marked on increasing the degree of methylation of the amide; *i.e.* FMD < MFD < DMF < MAC < DMAC.

The existence of a maximum can be explained in terms of two competing effects in the ion-exchange model. Added SDS increases the relative concentrations of PEN and H$^+$ in the Stern layer, which increases the reaction rate, and the ascending branch of the curve is observed. As the concentration of SDS increases, more Na$^+$ ions, which are unreactive counterions, are present, competing with H$^+$ for the available sites in the Stern layer and inhibiting the reaction. The relative contributions of these competing factors results in the experimental maximum. The protonation of amides reduces the number of H$^+$ ions competing with Na$^+$ for the available sites at the micellar interface, and consequently the catalytic effect decreases. The reduction of the [PEN] in the micellar pseudophase by the presence of amides (see below) also decreases the catalytic effect observed experimentally.

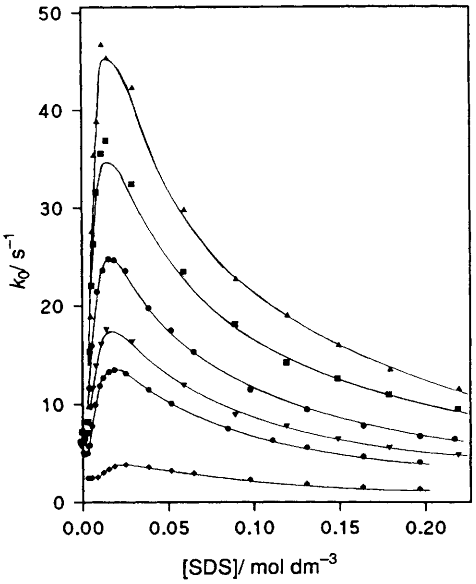


Fig. 5 Effect of [SDS] and [DMF] on the pseudo-first-order rate constant of the acid hydrolysis ([HCl] = 0.0127 mol dm^{-3}) of PEN at 25 °C and at [DMF] of (▲) 0.10; (■) 0.25; (●) 0.52; (▼) 0.75; (●) 1.04 and (◆) 2.44 mol dm^{-3}

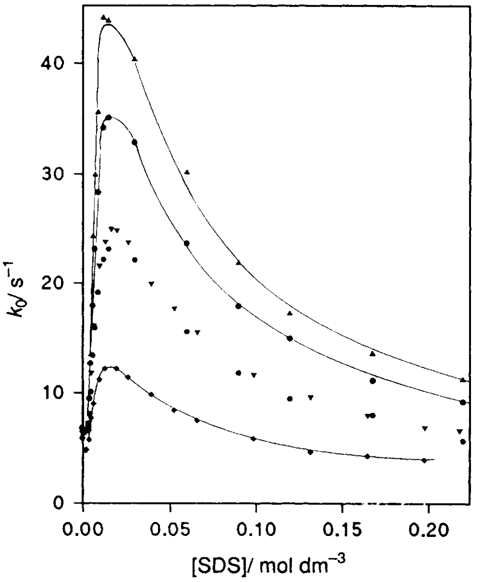


Fig. 6 Effect of [SDS] and the nature of amide on the pseudo-first-order rate constant of the acid hydrolysis ([HCl] = 0.0127 mol dm^{-3}) of PEN at 25 °C and 0.5 mol dm^{-3} of (▲) FMD, (●) MFD, (▼) DMF, (●) MAC and (◆) DMAC

According to the procedure previously described,[8] the kinetic results of the hydrolysis of PEN in aqueous hydrochloric acid of SDS micelles were analysed quantitatively using the simple pseudophase ion-exchange model. This treatment involves the following: (1) partitioning of PEN between micellar and aqueous phase, that is, $\mathrm{PEN_w} + \mathrm{SDS_m} \rightleftarrows \mathrm{PEN_m}$, where K_s^N is the corresponding equilibrium constant determined as 79 mol^{-1} dm^3 in pure SDS micelles;[25] (2) selective ion exchange between the reactive ions H$^+$ and the inert counterion of the surfactant Na$^+$; $\mathrm{Na_w^+} + \mathrm{H_m^+} \rightleftarrows \mathrm{Na_m^+} + \mathrm{H_m^+}$, whose equilibrium constant $K_{\mathrm{Na}}^{\mathrm{H}}$ varies over a typical range of 0.6–1;[17] (3) independent reactivities in the micellar (k_2^{m}) and aqueous (k_2^{w}) phases and, finally, (4) the reduction of [H$^+$] as a consequence of the protonation of amides. In line with this formulation the present system can be described by eqn. (5).

$$k_0 = \frac{K_{\mathrm{AH}}^{(\mathrm{ap})}}{K_{\mathrm{AH}}^{(\mathrm{ap})} + [\mathrm{A}]_{\mathrm{t}}}\,\frac{k_2^{\mathrm{w}}[\mathrm{H}^+]_{\mathrm{t}} + \{(k_2^{\mathrm{m}}/\bar{V})K_{\mathrm{s}}^{\mathrm{N}} - k_2^{\mathrm{w}}\}m_{\mathrm{H}}[\mathrm{SDS}]_{\mathrm{m}}}{1 + K_{\mathrm{s}}^{\mathrm{N}}[\mathrm{SDS}]_{\mathrm{m}}} \qquad (5)$$

Here, $K_{\mathrm{AH}}^{(\mathrm{ap})}$ refers to the apparent acidity constant of amides in the presence of SDS micelles;[8] $\bar{V}$ is the volume of the micellar pseudophase per mole of micellized surfactant, which has been estimated as 0.14 dm^3 mol^{-1} by Bunton *et al.*[26] when the reaction zone of the micellar pseudophase is identified with the Stern layer; and $m_{\mathrm{H}} = [\mathrm{H}^+]_{\mathrm{m}}/[\mathrm{SDS}]_{\mathrm{m}}$ can be calculated as described in the literature.[27]

Adapting the data in this way is possible if $K_{\mathrm{AH}}^{(\mathrm{ap})}$ does not vary appreciably with [SDS]. Fig. 7 presents the variation of k_0 with [DMAC] at three different SDS concentrations. In this range of amide concentration the effect of decreasing the relative permittivity of the medium is not appreciable; therefore the reduction of k_0 as [DMAC] increases is due to the reduction of [H$^+$] resulting from the protonation of DMAC. The degree of protonation, *i.e.* $K_{\mathrm{AH}}^{(\mathrm{ap})}$, is independent of [SDS]; therefore, the ratio of k_0 values determined in the absence and in the presence of 1.0 mol dm^{-3} of DMAC is practically independent of [SDS], (see Table 3). From these experimental results and following the same analytical procedure as for the study of the reaction in water, we obtain the values of $K_{\mathrm{AH}}^{(\mathrm{ap})}$

Table 3 Experimental conditions and apparent acid ionization constants of amides $K_{AH}^{(ap)}$ obtained at fixed [SDS] by studying the influence of [amide]

amide	[SDS] /mol dm^{-3}	$K_{AH}^{(ap)}$ /mol dm^{-3}	$k_0/k_0^{1M\,a}$	$k_0/k_0^{1M\,b}$
FMD	0.010	1.03	1.9	1.8
FMD	0.10	1.23	1.8	—
MFD	0.010	0.750	2.2	1.4
MFD	0.10	0.813	2.9	—
DMF	0.005	0.312	4.3	1.6
DMF	0.010	0.320	4.8	—
DMF	0.10	0.358	3.9	—
MAC	0.010	0.255	5.4	1.9
DMAC	0.006	0.175	8.4	2.75
DMAC	0.024	0.142	8.3	—
DMAC	0.10	0.155	8.9	—

The ratio of the observed rate constants obtained in the absence and in the presence of 1 mol dm^{-3} of amide in [a] aqueous micellar solutions of SDS and [b] in water.

reported in the same Table. The consistency of $K_{AH}^{(ap)}$ values at varying [SDS] is a consequence of the experimental conditions used, in particular [amide] $\geqslant 10[H^+]$, and the nature of the amide cations,[28] which bind to the SDS micellar surface more than do the H^+ or Na^+ ions. However, the relative increase in the basic character of amides in the presence of SDS micelles becomes greater as the structure of the molecule becomes more complicated. The larger the amide molecule, the greater the polarizability of the amidonium cation. This fact implies a greater association to the micellar surface and subsequent reduction of the H^+ concentration in the micellar surface, which explains the comparative effects of the different amides shown in Fig. 6. Table 3 also reports the relative inhibition effect (k_0/k_0^{1M}) found with the other amides in water and in the presence of SDS micelles at [amide] where no medium effects need be considered. Clearly, one can see that the capability of micelles to increase the basic character of amidonium cations is augmented with the polarizability of the latter.

Once $K_{AH}^{(ap)}$ was shown not to vary with [SDS], the experimental kinetic data were fitted to eqn. (5) by the simulation procedure described elsewhere,[27b,c] that followed in other studies in which we applied the ion-exchange model. Constant values of β (determined as previously indicated and reported in Table 2), c.m.c. (determined either kinetically or by fluorescence measurements) and k_w ($= k_2^w K_{AH}[H^+]_t/\{K_{AH} + [A]_t\}$ the experimental first-order rate constant obtained in water in the presence of amide) were used to estimate the values of K_s^N, K_{Na}^H and $\gamma(k_2^m/\bar{V})$, being $\gamma = K_{AH}^{(ap)}/(K_{AH}^{(ap)} + [A]_t)$. We found that values of K_{Na}^H in the range 0.7–0.8 all gave very good fits to the experimental points, yielding quite similar values of the optimized parameters. We therefore chose $K_{Na}^H = 0.75$ in every case.

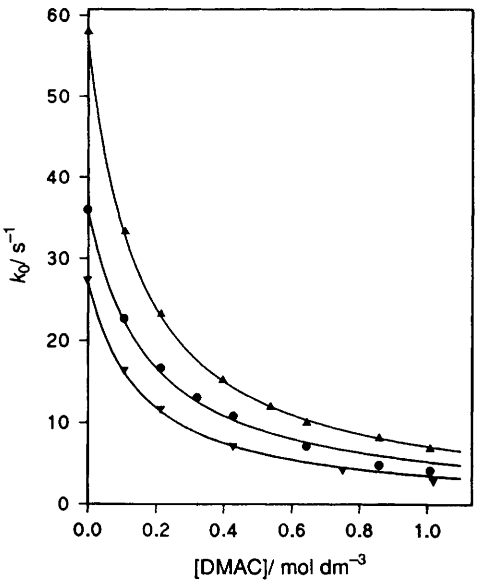


Fig. 7 Effect of DMAC on the pseudo-first-order rate constant of the acid hydrolysis ([HCl] = 0.0127 mol dm^{-3}) of PEN at [SDS] of (▲) 0.012, (●) 6×10^{-3} and (▼) 0.10 mol dm^{-3}

Table 4 lists the values of the fixed parameters used in the

Table 4 Values of rate and equilibrium constants used and optimized on fitting experimental data to eqn. (5) by a simulation procedure for the acid hydrolysis of PEN at [HCl] = 1.27×10^{-2} mol dm^{-3} in the presence of SDS micelles and amides

[amide][a]	k_w/s^{-1}	k_1/mol^{-1} dm^3 s^{-1}	β	$\gamma(k_2^m/\bar{V})$ s^{-1}	γ^b	k_2^m/mol^{-1} dm^3 s^{-1}	K_s^N/mol^{-1} dm – 3
				FMD			
0	8.2	646	0.80	320 ± 2	1.0	45	79 ± 1
0.25	6.15	484	0.77	296 ± 3	0.81	51	70 ± 2
0.50	5.90	465	0.77	263 ± 5	0.69	54	76 ± 3
				MFD			
0.25	7.35	579	0.77	258 ± 4	0.75	48	59 ± 2
0.50	6.95	547	0.75	222 ± 6	0.61	51	50 ± 3
1.0	5.85	464	0.71	166 ± 5	0.43	54	42 ± 2
				DMF			
0.10	7.81	623	0.77	269 ± 5	0.77	49	67 ± 3
0.25	7.35	579	0.75	215 ± 5	0.58	52	66.5 ± 3
0.52	6.55	516	0.70	159 ± 2	0.39	56	55 ± 2
0.75	6.13	483	0.68	130 ± 3	0.31	58	42 ± 2
1.04	5.30	417	0.68	102 ± 2	0.25	58	40 ± 1
2.44	2.80	221	0.64	42 ± 1	0.12	48	22 ± 1
				MAC			
0.25	7.52	596	0.75	198 ± 4	0.50	55	63 ± 3
0.50	6.55	512	0.72	149 ± 3	0.33	63	52 ± 2
1.0	4.63	365	0.63	99 ± 2	0.20	69	29 ± 2
				DMAC			
0.25	6.75	532	0.75	144 ± 3	0.42	48	56 ± 3
0.54	4.96	391	0.70	81 ± 2	0.23	49	43 ± 2
1.0	3.28	258	0.65	43.9 ± 0.6	0.14	45	39 ± 2

[a] Amide concentrations in mol dm^{-3}; [b] $\gamma = K_{AH}^{(ap)}/(K_{AH}^{(ap)} + [\text{Amide}])$.

fits, as well as the optimized values of K_s^N and $\gamma(k_2^m/\bar{V})$. The errors reported for these parameters correspond to those evaluated in the fitting process of the experimental data. The root-mean-square deviation of the experimental points from the model was used as the standard parameter of goodness of fit and in every case was lower than 3.5%. Solid lines on Figs. 5 and 6 show the theoretical fits to the experimental points.

The results obtained for K_s^N in the presence of formamide barely differ from the value determined in water. The presence of the other amides increases the solubility of PEN in water, and thus reduces the value of K_s^N. This effect increases both with amide concentration and the degree of amide methylation. DMF and DMAC reduce the relative permittivity of water mixtures. This would increase the solubility of PEN in water, a very hydrophobic species that dissolves better in a low-polarity solvent. Nevertheless, MFD and MAC, which increase the polarity of water mixtures, show the same effect: the presence of both amides greatly increases the water solubility of PEN. A possible explanation for this fact can be found in the properties of amides that disrupt the long-range order of water, as was found with ureas and, in general, with any non-electrolyte soluble in water. Nevertheless, tetramethylurea exhibits the greatest effect for water structure-breaking or hydrophobic-groups solvating.[8]

Additionally, one can see that the presence of amides diminishes the observed rate constant obtained both in water, k_w, and in the micellar interface, $\gamma(k_2^m/\bar{V})$, as a consequence of the reduction of the effective $[H^+]$ because of their protonation. Consequently, from the value of $K_{AH}^{(ap)}$ determined for each amide in the presence of SDS micelles, one may determine the values of γ reported in Table 4. These values, together with $\bar{V}$, the molar volume of the micellar interface where the reaction takes place, imply the bimolecular reaction constants at the micellar interface, k_2^m, listed in Table 4. As one can see, the values do not differ very much from those determined in water in the absence of amides. This result could indicate that the presence of amides does not modify the polarity of the micellar interface, at least not in a significant manner under the experimental conditions of this study. Fluorescence measurements support this idea. In this sense, the I_I/I_{III} ratio (fluorescence intensities of pyrene's first and third vibronic peaks) varies in the range 1.07–1.11 at $[SDS] = 0.05$ mol dm^{-3} in the presence of 0.5 or 1.0 mol dm^{-3} of the several amides studied here. This value is, moreover, that found in pure SDS solutions, whereas the relative peak intensities in pure DMF or MFD are 1.82 and 1.54, respectively.[18] If a considerable [amide] were at the micellar interface, the polarity of the same should vary, and consequently, the I_I/I_{III} ratio. The kinetic results also indicate a minor amide effect on the structure of SDS micelles.

Conclusions

Study of the influence of amides on the acid hydrolysis of 1-phenylethylnitrite provides a simple and accurate method for determining the pK_a of amides. This study constitutes the first indirect kinetic method for measuring these controversial data, in water as well as in the presence of the anionic micelles of SDS. The basicity of the amides in water is shown to increase in the presence of SDS micelles, as has been found in the case of secondary aliphatic amines.[4f,5e] On the other hand, the presence of amides shows only minor effects on the structure of SDS micelles; thus, neither the c.m.c., the aggregation number, the fractional micellar charge neutralized (β), nor k_2^m values are shown to vary appreciably in the presence of amide. The main observed effect is a greater solubility in water of PEN, a very hydrophobic species, in the presence of amides, which can be attributed to the properties of amides that break the structure of water or solvate hydrophobic groups, as do ureas, with their denaturant properties

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