

Cite this article

Pavlov RV, Valeeva FG, Gaynanova GA, Kuznetsov DM and Zakharova LY
Aggregation of morpholinium surfactants with amino alcohols as additives: a close look.
Surface Innovations,
<https://doi.org/10.1680/jsuin.22.00006>

Research Article

Paper 2200006
Received 21/01/2022; Accepted 05/04/2022

ICE Publishing: All rights reserved

Aggregation of morpholinium surfactants with amino alcohols as additives: a close look

Rais V. Pavlov MSc

PhD candidate, Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, Kazan, Russia (Orcid:0000-0002-0559-1095) (corresponding author: rais.pavlov@iopc.ru)

Farida G. Valeeva PhD

Researcher, Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, Kazan, Russia

Gulnara A. Gaynanova PhD

Senior Researcher, Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, Kazan, Russia (Orcid:0000-0002-0406-4066)

Denis M. Kuznetsov PhD

Junior Researcher, Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, Kazan, Russia (Orcid:0000-0002-9572-3708)

Lucia Ya. Zakharova PhD

Full Professor and Chief Researcher, Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, Kazan, Russia (Orcid:0000-0002-2981-445X)

Mono-, di- and triethanolamine in combination with methylmorpholinium and hydroxyethylmorpholinium surfactants were investigated for their aggregation and solubilizing properties. A co-operative behavior of the solubilization by mixed surfactant–ethanolamine systems is described. Ethanolamines strongly affect pH and lead to Orange OT phenolic group deprotonation and subsequent increase in aqueous/micellar solubility. The morpholinium surfactant micelles reduce the pK_a of the Orange OT phenolic group, enabling its deprotonation at the earlier stages of medium alkalization. The obtained surfactant–ethanolamine mixtures can solubilize very large amounts of hydrophobic dye, which can then be triggered to precipitate through acidification.

Keywords: pH/self-assembly/surface chemistry

Notations

A_{\min}	surface area per molecule
a	polar head surface area
$C_{\text{additive}}, C_{\text{HC}}, C_{\text{MEA}}$	concentration
$C_{\text{MS(OH)-16}}$	concentration of MS(OH)-16
$C_{\text{MS-16}}$	concentration of MS-16
D	optical density
G_{\min}	minimal free energy of the interface
l	optical path length
l	surfactant tail length
λ	wavelength
N_A	Avogadro's number
n_c	number of carbon atoms in the surfactant tail
P	surfactant packing parameter
R	universal gas constant
S	solubilization capacity
S_1, S_2	conductivity plot slopes before and after the critical micellization concentration, respectively
T	absolute temperature
v	surfactant molecule volume
β	fraction of neutralized surfactant counterions
γ	fraction of neutralized surfactant counterions
Γ_{\max}	surface excess
ΔG_{ad}	free energy of adsorption
ΔG_{mic}	free energy of micelle formation
κ	conductivity
χ	mole fraction

1. Introduction

Solubilization of hydrophobic substances by surfactants is a phenomenon that has been used in households, agriculture and industry and has been extensively researched for many decades.^{1,2} Any surfactant can be used to solubilize hydrophobic molecules. Some surfactants are more capacious, and others can solubilize smaller amounts of the same compound. One of the promising types of surfactants based on the head group of morpholinium has recently been intensively studied. The presence of a heteroatom in the cyclic head group provides opportunities for establishing additional bonds in the processes of adsorption, micelle formation and solubilization.

Micellar systems based on morpholinium surfactants received much attention due to their various functional activities that can be tailored by both chemical modification of amphiphilic structures and admixing with components capable of inducing morphological transitions, shift in acid–base equilibrium and so on. One of the key directions of research in this area has been the introduction of biodegradable fragments into the structure of morpholinium surfactants.^{3–8} Chauhan *et al.*³ showed that the introduction of an ester group in the investigated surfactants decreases cytotoxicity toward C6 glioma cells significantly. A morpholinium surfactant with an ester fragment was used to form coacervates with sodium salicylate.⁴ A catanionic system was formed at a constant concentration of a morpholinium surfactant and a variable concentration of a hydrotropic additive (from 1 to 1000 mM), which led to the transformation of spherical aggregates to cylindrical ones, which were capable of encapsulating curcumin. Vesicles spontaneously formed in an aqueous catanionic system based on a morpholinium surfactant, 4-methyl-4-(2-(octyloxy)-2-oxoethyl) morpholine-4-ium bromide, and sodium dodecyl sulfate have been studied as a template for the synthesis of hollow silica nanospheres.⁵

Offprint provided courtesy of www.icevirtuallibrary.com
 Author copy for personal use, not for distribution

A series of surfactants with the same dodecyl tail and two ester bonds in the spacer, but with different head groups (piperidinium, pyrrolidinium, morpholinium and quaternary ammonium) was obtained by Bhadani *et al.*⁶ Morpholinium gemini surfactants showed a slightly higher critical micellization concentration (CMC) and lower viscosity compared with other amphiphiles. Morpholinium surfactants with an amide fragment showed CMC values lower than those of non-functionalized analogs due to the possibility of the formation of an intermolecular hydrogen (H) bond.⁷ An increase in the size of aggregates and a decrease in aggregation numbers and packing density with an increase in the length of the alkyl tail in the octyl–dodecyl–hexadecyl series were shown. It was shown by Bhadani *et al.*⁸ that at a concentration above 50 wt%, a morpholinium surfactant formed lyotropic liquid crystalline phases. Some studies found that morpholinium surfactants are less toxic compared with hexadecyltrimethylammonium bromide.^{9,10} Morpholinium surfactants have also been comprehensively studied by the authors' group in the past in terms of aggregation behavior and solubilization activity in individual solutions¹¹ and in the presence of additives (hydrotropes¹² and polymers¹³), catalytic effects¹⁴ in nucleophilic substitution reactions, lipoplex formation,¹⁵ corrosion inhibition and antimicrobial properties.¹⁶

An interesting research direction could involve combination of morpholinium surfactants with amino alcohols. Due to their buffering properties, some of them – monoethanolamine (MEA), diethanolamine (DEA) or triethanolamine (TEA) – are widely used in cosmetic products as acidity regulators, in the gas industry as carbon dioxide (CO₂) and hydrogen sulfide (H₂S) removers, in metalworking as corrosion inhibitors, in textile processing and in specialty cleaning formulations.¹⁷ Their fatty acid salts and a number of other derivatives are also used as surfactants and preservatives.^{18–20} For industrial applications, MEA and TEA are mainly used as rust inhibitors.²¹ TEA is also utilized in cosmetics; however, instances of allergic reactions to topical application of TEA are known, and DEA cannot be used in cosmetics due to possible carcinogenicity.²¹ TEA is also applied to modulate cement properties, by affecting the hydration process of different mineralogical phases in cement.²² Due to high basicity, MEA can also be used for the formation of biocompatible

salt forms of acidic drugs such as piroxicam or meloxicam, which are characterized by increased solubility and bioavailability.^{20,23,24}

Ethanolamines were used as counterions for anionic surfactants, which were investigated for their ability to form liquid crystals.²⁵ Another study showed that MEA at low concentrations (below 10–20 wt%) increased the area per surfactant molecule on the air–water interface, which led to lower interface saturation with amphiphilic molecules and less dense packing. At the same time, at low MEA concentrations, a decrease in CMC was observed for the studied imidazolium surfactant.²⁶ Overall, aggregation studies involving mixtures of surfactants and ethanolamines are rare. However, considering the wide usability and applicability of ethanolamines, their combination with morpholinium surfactants may be of interest. In this work, the aim was to investigate morpholinium surfactants *N*-hexadecyl-*N*-methylmorpholinium bromide (MS-16) and *N*-hexadecyl-*N*-hydroxyethylmorpholinium bromide (MS(OH)-16) in composition with ethanolamines (Figure 1), to outline the physicochemical and self-assembly aspects and potential applications of their combinations.

2. Experimental section

2.1 Materials

Orange OT (OOT) was obtained from ChemCruz; MEA, DEA and TEA were obtained from Acros Organics; and Milli-Q ultrapurified water (18.2 MΩ cm) was obtained using a Millipore Direct-Q 5UV apparatus. Morpholinium surfactants MS-16 and MS(OH)-16 were synthesized as described in the paper by Yackevich *et al.*¹⁴

2.2 Tensiometry

The measurements were done using a Kruss K6 (Germany) tensiometer using the Du Noüy ring detachment method. The platinum (Pt) ring was rinsed with ethanol, and the ethanol was wiped off and briefly left to evaporate before each measurement. Every sample (10 ml) was measured repeatedly to ensure value consistency between at least four consecutive measurements. The temperature of the samples was maintained as 25°C using a water-circulating jacket attached to a thermostat. The instrumental error was within 0.3 mN/m.

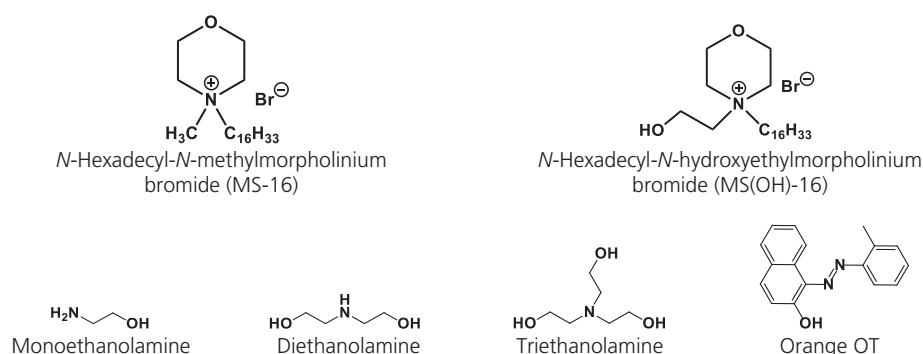


Figure 1. Structures of the studied compounds

Offprint provided courtesy of www.icevirtuallibrary.com
Author copy for personal use, not for distribution

2.3 Conductometry

The measurements were done using an InoLab Cond7110 conductometer, which was calibrated using a 0.01 potassium chloride (KCl) solution. The temperature of the samples (10 ml) was maintained as 25°C using a water-circulating jacket attached to a thermostat. The data were approximated using an antiderivative of a Boltzmann sigmoid as described in the paper by Carpena *et al.*,²⁷ which allowed extraction of the slopes of the graph before and after CMC, as well as the CMC value.

2.4 Potentiometry

A freshly calibrated Hanna Instruments pH 211 apparatus was used. Samples (10 ml) under constant stirring (360 revolutions/min) were probed with the pH-measuring glass electrode. Each sample was equilibrated under stirring for exactly 4 min before value recording. The measurements were conducted at an ambient temperature of 25°C.

2.5 Spectrophotometry

Ultraviolet/visible absorption spectra were recorded on a Specord 250 Plus (Germany) device using thermostated cells controlled by Peltier elements (Analytik Jena, Germany) at 25°C in quartz cuvettes. The spectra were recorded using 1 nm monochromator slits in the range 190–800 nm. For solubilization, excessive amounts of OOT (15–30 mg) were added to surfactant samples (2 ml) of different concentrations, which were then briefly vortexed (15–20 min) and left in the dark at ambient temperature for 48 h to reach equilibrium before spectrophotometric analysis. At the time of measurement, Millipore polytetrafluoroethylene syringe filters (0.22 µm pores) were used to ensure complete separation of the liquid phase from any undissolved OOT before the sample was placed in a cuvette. For strongly absorbing samples, thinner cuvettes were used, and if necessary, dilution in Milli-Q water was performed. Spectra were analyzed for absorbance at 495 nm using an absorption coefficient of 17 400 l mol⁻¹ cm⁻¹. Solubilization capacity values were determined as the slope of the plot region after the CMC.²⁸ For the evaluation of pH-dependent OOT dissolution and precipitation, 100 mM MEA and 2.7 mM MS-16 compositions were prepared, excessive OOT was added and the mixture was equilibrated and filtered before spectrophotometric analysis as described earlier.

2.6 Thermodynamic parameters

Tensiometric and conductometric data were used in combination to derive thermodynamic parameter values. Tensiometric data provide information to derive surface excess (Γ_{\max}) and equilibrium area per surfactant monomer (A_{\min}) by treating the descending part of the surface tension isotherm with the Gibbs absorption equation:²⁹

$$1. \quad \Gamma_{\max} = -\frac{1}{2.303nRT} \times \lim_{C \rightarrow C_{\text{cmc}}} \frac{d\sigma}{d \log C}$$

Here, n is equal to 2, R is the universal gas constant in joules per mole per kelvin, T is the absolute temperature in kelvin and the limit is found as the slope of surface tension isotherm in $\log C$ coordinates

at the closest point to the CMC. This yields the surface excess in moles per 1000 m² if σ is in millinewtons per meter. The surface area per surfactant molecule at the interface can then be obtained:

$$2. \quad A_{\min} = \frac{10^{21}}{N_A \Gamma_{\max}}$$

where N_A is Avogadro's number and A_{\min} is in square nanometers.²⁹

Conductometric data allow calculation of β , the fraction of neutralized surfactant counterions that are bound to the micelles as in the publication by Rosen:³⁰

$$3. \quad \beta = 1 - S_2/S_1$$

where S_1 and S_2 are conductivity plot slopes before and after the CMC, respectively. The free energy of micelle formation can then be found as

$$4. \quad \Delta G_{\text{mic}} = RT(1 + \beta) \ln \text{CMC} - 0.5RT \ln 2$$

where CMC is expressed as a molar concentration.³¹ Finally, the free energy of surfactant adsorption on the air–water interface is found as in the publication by Rosen:²⁹

$$5. \quad \Delta G_{\text{ad}} = \Delta G_{\text{mic}} - 6.023\pi_{\text{CMC}}A_{\min}$$

The minimum free energy was calculated using γ_{CMC} as surface tension at CMC as described in the papers by Rub *et al.*:^{32,33}

$$6. \quad G_{\min} = \gamma_{\text{CMC}}A_{\min}N_A$$

The critical packing parameter was found as described by Tanford:³⁴

$$7. \quad P = v/(la)$$

where the surfactant molecule volume v in cubic nanometers is calculated as $v = 0.0274 + 0.0269n_c$ and the surfactant tail length in nanometers is $l = 0.154 + 0.1265n_c$. n_c is the number of carbon (C) atoms in the surfactant tail. a is the polar head surface area, which is critically dependent on solution conditions; most commonly, it is taken equal to A_{\min} .

3. Results and discussion

3.1 CMC and aggregation

Firstly, a basic tensiometric analysis of the surface activity of morpholinium surfactants with and without any additives (Figure 2)

Offprint provided courtesy of www.icevirtuallibrary.com
Author copy for personal use, not for distribution

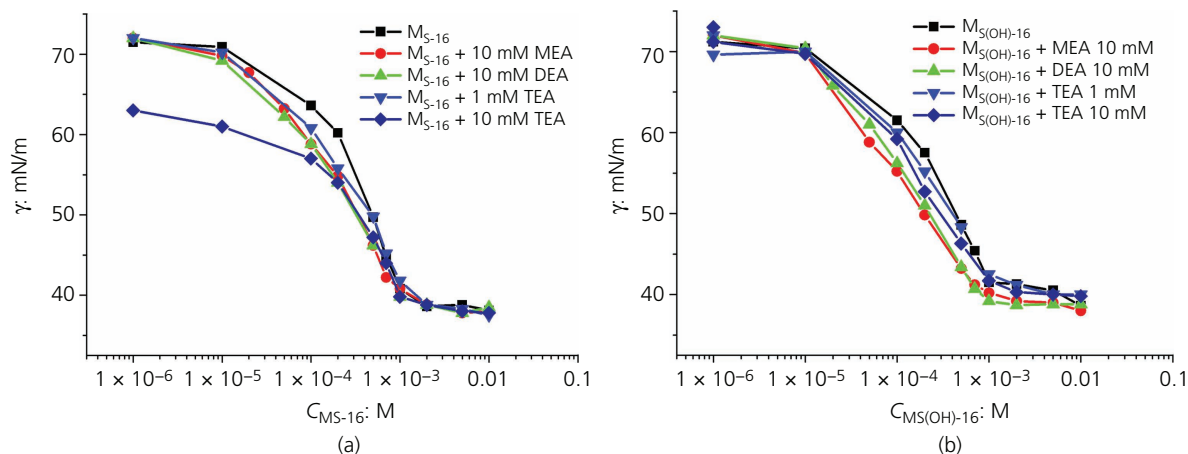


Figure 2. Surface tension isotherms of (a) MS-16 and (b) MS(OH)-16 with additives, 25°C

was carried out. Among ethanolamines, TEA had the least effect on the aggregation threshold: the CMC determined for MS(OH)-16 in the presence of additives is within the CMC error determined for individual MS(OH)-16 and is about 1.0 mM (Figure 2(b)). In the presence of MEA and DEA, a small decrease in the aggregation threshold to 0.7–1.0 mM is observed. This may be observed because of co-operative accumulation of ethanolamines and surfactants on the interface, as evident from the equilibrium molecule cross-sectional area increase in Tables 1 and 2.

Some of the isotherms are shifted more to the left along the concentration axis – for example, MEA and DEA isotherms. Such data indicate more active adsorption of surfactants on the water–air interface, which is also supported by the increase in molecular areas. The most significant effect is observed for MEA with hydroxyethylated MS(OH)-16, and in the case of TEA at concentrations of 1 and 10 mM, this effect is minimal. In general,

surface tension at each concentration point is higher for individual surfactants (square plot on top) than for mixtures. These data suggest the presence of a certain degree of co-operativity in the process of adsorption of surfactant molecules at the water–air interface in the presence of MEA and DEA. Since these additives themselves in the studied concentrations do not have a surface activity comparable with the surface activity of typical surfactants but at the same time decrease the surface tension in the presence of surfactants, it is very likely that they can accumulate in the surface layer, which leads to lower surface tension.

Other informative parameters of surfactants are the pC20 value, which characterizes the surface activity, and minimal free energy G_{\min} (Tables 1 and 2). The pC20 value is a characteristic surfactant parameter that shows how much surfactant is needed to lower the surface tension by 20 mN/m. pC20 slightly increases with additives; the strongest effect is observed for MEA and

Table 1. Thermodynamic parameters of adsorption and micelle formation for the MS-16 surfactant with different additives

Composition	ΔG_{mic} : kJ/mol	ΔG_{ad} : kJ/mol	G_{min} : kJ/mol	Γ_{max} : $\times 10^6$ mol/m ²	A_{min} : nm ²	CMC: ^a mM	pC20	P
MS-16	−31.4	−43.9	16.7	2.45	0.68	1.0 ± 0.3	6.39	0.31
MS-16 + MEA 10 mM	−29.7	−46.4	22.4	1.83	0.91	0.8 ± 0.3	6.57	0.23
MS-16 + DEA 10 mM	−31.6	−49.8	23.7	1.67	0.99	1.0 ± 0.3	6.60	0.21
MS-16 + TEA 1 mM	−27.6	−45.0	23.9	1.75	0.95	1.0 ± 0.3	6.45	0.22
MS-16 + TEA 10 mM	−30.8	−48.3	22.8	1.74	0.95	1.0 ± 0.3	6.58	0.22

^a The measurement error is estimated based on the character of the inflection on the surface tension isotherms

Table 2. Thermodynamic parameters of adsorption and micelle formation for the MS(OH)-16 surfactant with different additives

Composition	ΔG_{mic} : kJ/mol	ΔG_{ad} : kJ/mol	G_{min} : kJ/mol	Γ_{max} : $\times 10^6$ mol/m ²	A_{min} : nm ²	CMC: ^a mM	pC20	P
MS(OH)-16	−30.0	−45.3	20.7	1.99	0.83	1.0 ± 0.3	6.45	0.25
MS(OH)-16 + MEA 10 mM	−29.8	−52.7	30.0	1.33	1.24	0.9 ± 0.3	6.82	0.17
MS(OH)-16 + DEA 10 mM	−33.6	−52.5	24.3	1.62	1.03	0.7 ± 0.3	6.76	0.20
MS(OH)-16 + TEA 1 mM	−29.2	−49.1	27.6	1.53	1.08	1.0 ± 0.3	6.51	0.20
MS(OH)-16 + TEA 10 mM	−30.8	−50.9	27.4	1.52	1.09	1.0 ± 0.3	6.66	0.19

^a The measurement error is estimated based on the character of the inflection on the surface tension isotherms

Offprint provided courtesy of www.icevirtuallibrary.com
Author copy for personal use, not for distribution

DEA. The G_{\min} values for individual surfactants are lower compared with those for mixtures with amino alcohols, while the effect of the nature of additives is negligible.

As seen on the conductometric plots (Figure 3), while all the obtained curves are characteristic of a very similar value of CMC, those with MEA have the highest conductivity values, probably due to highest mobility and basicity of the additive molecule. TEA samples are at the same level as the individual surfactant, with DEA taking an intermediate position (Table 3).

CMC values obtained using conductometry are slightly more accurate than tensiometric ones due to the ease of data approximation, and some comparisons can be made. Among the combinations with MS-16, the lowest CMC is observed for the mixture with DEA at 0.9 mM. The rest of the values are roughly in the range 1.1–1.2 mM. The lowest aggregation threshold for MS(OH)-16 is observed for a mixture with TEA of about 1.1 mM; the values for the remaining mixtures are about 1.2–1.4 mM. The highest CMC value is observed for the individual MS(OH)-16 (1.40 mM) and a mixture with MEA (1.39 mM). Considering tensiometric and conductometric CMC measurements overall, it can be concluded that no significant difference in the aggregation thresholds is present. This indicates that on aggregate formation in mixed systems, the additives are not likely participating in the self-assembly. If there were beneficial interactions of the amino alcohols with surfactants, a significant effect on the CMC or ΔG_{mic} would have been observed for such systems.

The combination of tensiometric and conductometric data yields the thermodynamic parameters of micellization and adsorption at the air–water interface (Tables 1 and 2). Addition of any amino alcohol leads to an increase in area per molecule A_{\min} and a decrease in surface concentration Γ_{\max} . The same was previously observed with a different cationic surfactant.²⁶ These values are obtained at the same surfactant concentrations, since all surfactant mixtures with ethanolamines have very similar CMCs. Therefore, a decrease in surface concentration of surfactant monomers (Γ_{\max}) indicates an increase in concentration in the bulk in the presence of ethanolamines, which may be explained by a variety of possible intermolecular interactions available for surfactants and amino alcohols in the solution. The hydroxyethyl surfactant MS(OH)-16 is characterized by larger A_{\min} values compared with the MS-16, which could be explained by a larger head group of MS(OH)-16, and its better solubility in bulk due to an additional polar group. Evaluation of packing parameter value (Tables 1 and 2) for each of the compositions shows that in every studied mixture, the surfactants are expected to form spherical micelles. The addition of ethanolamines decreases the packing parameter for both surfactants MS-16 and MS(OH)-16.

3.2 Solubilization of OOT

Using the hydrophobic dye OOT, studies of the solubilizing ability of compositions based on morpholinium surfactants with various additives toward the hydrophobic probe were carried out. The results are shown in Table 3; plots and spectra can be seen in

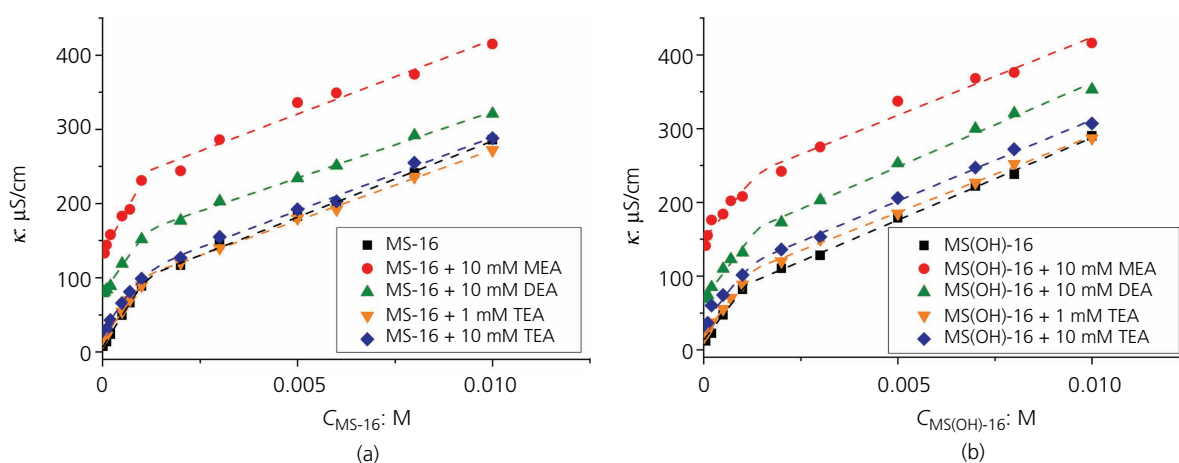


Figure 3. Conductivity plots of (a) MS-16 and (b) MS(OH)-16 with additives, 25°C

Table 3. Summary of CMC and OOT solubilization capacity values for MS-16 and MS(OH)-16 surfactants and additives

Additive	MS-16 CMC ^a conductometry: mM	S ^a for MS-16	MS(OH)-16 CMC ^a conductometry: mM	S ^a for MS(OH)-16
—	1.17 ± 0.26	0.019 ± 0.002	1.40 ± 0.40	0.037 ± 0.007
MEA (10 mM)	1.13 ± 0.18	0.036 ± 0.004	1.39 ± 0.18	0.057 ± 0.004
DEA (10 mM)	0.90 ± 0.46	0.038 ± 0.005	1.19 ± 0.12	0.048 ± 0.005
TEA (1 mM)	1.17 ± 0.07	0.043 ± 0.001	1.28 ± 0.10	0.034 ± 0.002
TEA (10 mM)	1.09 ± 0.09	0.044 ± 0.001	1.10 ± 0.33	0.040 ± 0.001

^a The measurement error is standard deviation of approximation

Offprint provided courtesy of www.icevirtuallibrary.com
Author copy for personal use, not for distribution

Figures S1–S10 in the online supplementary material. Among the compositions based on MS-16, the highest solubilization capacity of $0.044 \text{ mol}_{\text{OOT}}/\text{mol}_{\text{MS-16}}$ is observed for compositions with the addition of TEA at concentrations of 1 and 10 mM. The lowest value corresponds to the individual solution of MS-16; the rest of the additives are at the same level, increasing the solubilization capacity to $0.031\text{--}0.038 \text{ mol}_{\text{OOT}}/\text{mol}_{\text{MS-16}}$. Thus, the use of all additives increases solubilization for MS-16 by more than 60%, and in the case of TEA, solubilization increases by 125% even with the addition of only 1 mM TEA.

In the case of compositions with MS(OH)-16, the head group of which has a hydroxyethyl fragment, the solubilization capacity value for an individual surfactant solution is almost twice as high as for a non-hydroxyethylated analog and is $0.037 \text{ mol}_{\text{OOT}}/\text{mol}_{\text{MS(OH)-16}}$. This is due to the presence of a hydroxyl group, which can participate in additional interactions with solubilized OOT. In mixed compositions with MS(OH)-16, the highest solubilization capacity was shown by a mixture with 10 mM MEA, reaching a value of $0.057 \text{ mol}_{\text{OOT}}/\text{mol}_{\text{MS(OH)-16}}$, which is the maximum among all the compositions studied in this work. Addition of TEA at 1 or 10 mM insignificantly affects solubilization capacity, and DEA increases it by 30% and MEA by 54%. These effects correspond well to the basicity of each amino alcohol.

With MEA, the solubilization graphs (Figure 4) contain a characteristic region at concentrations near the aggregation threshold, the slope of which is steeper than that of the main part of the solubilization curve (after CMC). This is typical evidence of joint aggregate formation as is often observed for mixed systems and particularly surfactant–polymer compositions.² The early steep region of solubilization plots characterizes the systems with very high solubilization capacity values of around $0.1 \text{ mol}_{\text{OOT}}/\text{mol}_{\text{Surfactant}}$, which is 2.5–3.0 times higher than for the MS-16 individual surfactant. In this region, as few as ten surfactant molecules are sufficient to solubilize one OOT molecule.

The slope of the solubilization plot also indicates some sort of solubilizing aggregate presence for compositions in the concentration range 0.1–0.5 mM, which are more capacious for the substrate compared with conventional micelles that start to form after 1 mM of surfactant concentration.

To evaluate the effect of ethanolamines on the solubilization capacity, a different approach was also used, where the surfactants were fixed at a concentration of 2.7 CMC and MEA concentrations were varied. The main cause of solubilization increase is connected to the high basicity of amino alcohols, and MEA, being the most basic of the three, was chosen for further work. Solubilization of OOT was checked at different concentrations of added MEA, and very high solubilization capacities were observed (Figure 5).

3.3 pH-dependent OOT solubility in micellar solution

Further evaluation of the effect of MEA and TEA concentrations on the solubilizing activity of MS-16 and MS(OH)-16 surfactants was done, and a very strong effect was observed for MEA, but not TEA. This is most likely due to higher basicity of MEA ($\text{p}K_{\text{a}} = 9.5$) against that of TEA ($\text{p}K_{\text{a}} = 7.8$), which causes OOT hydroxyl deprotonation. Under alkaline conditions, the substrate molecule becomes an amphiphilic anion that readily participates in aggregate formation with the cationic surfactant.² Spectra of solubilized OOT are shown in Figure 5(a). With the increase in MEA concentration, the rise of a shoulder band at around 460 nm can be observed. OOT spectra in solvents of different polarities (hexane, ethanol, aqueous ethanol, and chloroform) do not demonstrate such distant hypsochromic shifts (Figure S11 in the online supplementary material), and pyrene fluorescent assay showed that MEA addition has no effect on the micropolarity of morpholinium surfactant micelles (Figure S12 in the online supplementary material). The changes in the OOT absorption spectrum are most likely caused by gradual formation of the OOT anionic form and correspond to its changed electron structure in

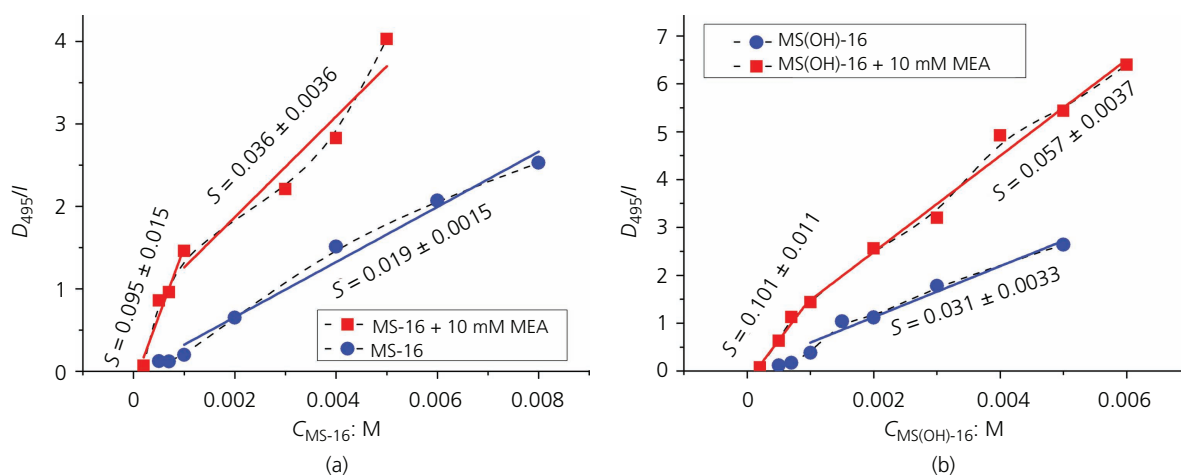


Figure 4. Effect of MEA concentration on solubilization of OOT as evaluated spectrophotometrically by using (a) MS-16 and (b) MS(OH)-16 micelles, 25°C

Offprint provided courtesy of www.icevirtuallibrary.com
Author copy for personal use, not for distribution

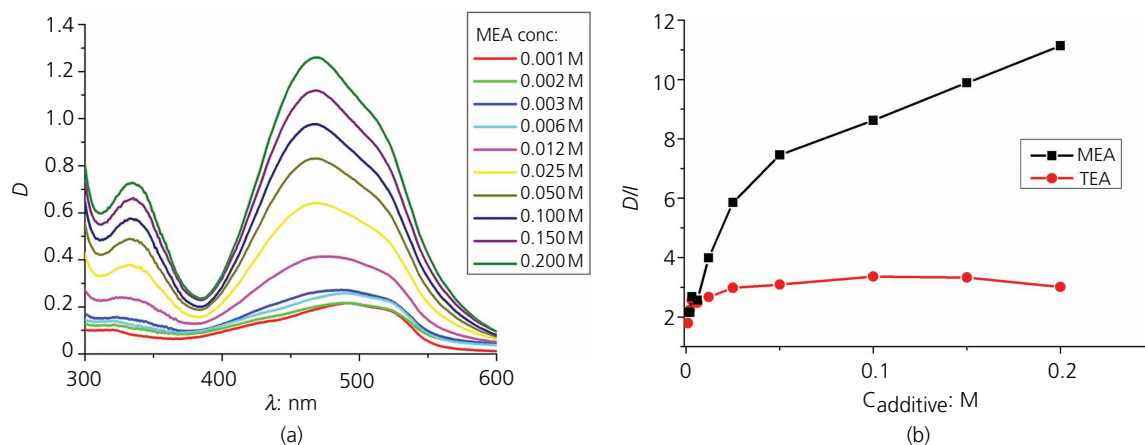


Figure 5. (a) OOT spectra in MS-16 micelles (2.7 mM) with increasing amount of MEA, $i = 0.1$ cm; (b) OOT absorption at 495 nm with increasing MEA or TEA concentration, 25°C

the deprotonated state. All of the above suggests that, although some evidence of MEA participation in surfactant aggregation is present, as described before, the nature of solubilization increase is purely caused by OOT dissociation under alkaline conditions.

OOT absorption can be plotted in relation to pH, since its solubility is connected to phenolic group deprotonation (Figure 6). Addition of MEA or sodium hydroxide (NaOH) without micelles does not lead to OOT dissolution (OOT absorption around 0.02–0.07). However, in the presence of cationic micelles, a very high OOT solubility can be achieved (absorption at 0.5–12 units). Hence, purely OOT dissociation granted by an alkaline medium is not sufficient to cause solubility at pH below 12, but the presence of cationic surfactants allows OOT molecules to act as a surfactant counterion and to form joint aggregates. It can be seen that an upward trend is observed much earlier for micellar OOT solutions, where a significant solubility increase starts at pH = 10, whereas for aqueous OOT, alkalization only slightly increases its solubility after pH 11.5. It is

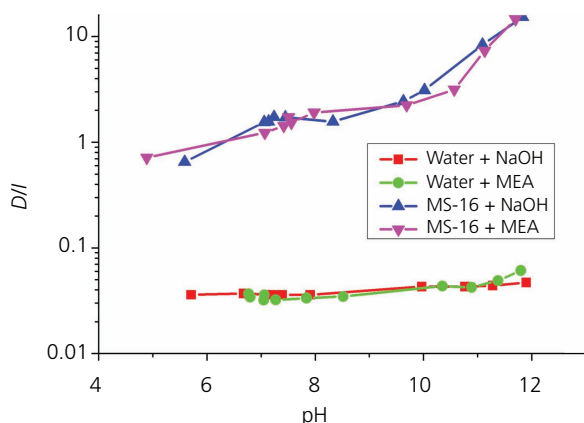


Figure 6. OOT absorption in MS-16 micellar solutions (at 2.7 mM) at different pH values induced by sodium hydroxide or MEA, 25°C

noteworthy that under basic conditions (pH > 9), solubilization occurred very rapidly, and liquid-phase coloration was observed after 15 min, in contrast to the slow process of OOT solubilization under neutral conditions, which takes more than 1 day to equilibrate.

Such a system can be manipulated into releasing the dissolved OOT with addition of acid. As expected, a small amount of hydrochloric acid (HCl) causes immediate clouding and precipitation of dye content, since the pH is lowered farther from OOT pK_a (Figure 7). At low hydrochloric acid concentrations (to the left of dashed line 1), precipitation happens very quickly, reaching more than 50%. Before the equilibrium point (dashed line 2), a slow increase in precipitated OOT is observed, after which (to the right of dashed line 2) the

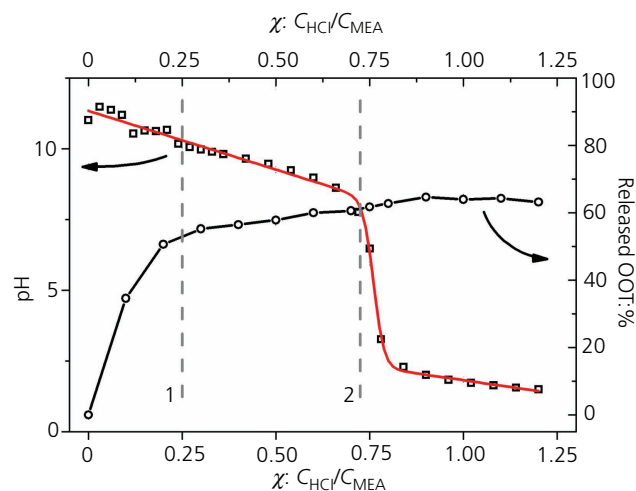


Figure 7. Left axis: potentiometric titration curve for OOT solubilized in MS-16 (2.7 mM) micelles under alkaline conditions induced by MEA (100 mM); right axis: OOT precipitation (in % compared with solubilization before acid addition) from mixed cationic MS-16 micelles after solubilization at pH 11.5, determined spectrophotometrically, 25°C; top and bottom axis: mole fraction χ

Offprint provided courtesy of www.icevirtuallibrary.com
Author copy for personal use, not for distribution

graph reaches a plateau. At this point, the pH is normalized; however, leftover dissolved micellar OOT is still more concentrated than what was observed for pure micellar solution. This may be explained by mixed aggregate formation of OOT molecules with MS-16 molecules, as was previously suggested.³⁵ Incomplete OOT precipitation is indirect evidence that mixed aggregates do form, which makes it possible to oversaturate cationic micelles with solubilized dye, most of which, on consecutive protonation, remains in the micellar phase without precipitation, leading to excessive OOT solubilization at a given pH. Further structural studies using microscopic or scattering methods are required to confirm directly that, however. Additional experimental work involving different cationic surfactant and hydrophobic substrate combinations with regard to pH conditions can be a promising route to discover novel application areas where cationic surfactants can be indispensable.

4. Conclusion

A morpholinium surfactant and its hydroxyethylated analog were investigated for their aggregation properties in the presence of ethanolamines – common industrial and cosmetic additives. No significant disruption of aggregate formation was observed with the addition of ethanolamines, and critical micelle concentration remained close to 1 mM for all the studied systems. Co-operative solubilization of OOT was observed with MEA addition for both surfactants MS-16 and MS(OH)-16. A very strong solubilizing effect toward the OOT hydrophobic probe can be achieved by MS-16 in the presence of 100 mM MEA, making it possible to dissolve 1 mol of OOT per 4 mol of the surfactant in aqueous solution due to probe deprotonation and mixed aggregate formation. The obtained compositions also showed responsiveness toward acidic stimuli, which allows temporary dissolution of OOT and release of more than half of it as precipitate with as low as 20 mol% of acid in relation to MEA concentration. This leads to formation of oversaturated mixed cationic micelles with leftover solubilized hydrophobic dye. All of the above suggests the potential of the cationic morpholinium surfactants to enhance the solubility of hydrophobic organic weak acids, which can find application in industry or cosmetics. By analogy, the same solubilization increase is expected in systems with anionic surfactants and basic poorly soluble organic substrates at acidic pH, which, however, requires experimental confirmation.

Acknowledgement

The authors are grateful for financial support from the government assignment for FRC Kazan Scientific Center of RAS.

REFERENCES

- Rangel-Yagui CO, Pessoa A and Tavares LC (2005) Micellar solubilization of drugs. *Journal of Pharmacy and Pharmaceutical Sciences* **8(2)**: 147–163.
- Tehrani-Bagha AR and Holmberg K (2013) Solubilization of hydrophobic dyes in surfactant solutions. *Materials* **6(2)**: 580–608, <https://doi.org/10.3390/ma6020580>.
- Chauhan V, Kamboj R, Singh Rana SP *et al.* (2015) Aggregation behavior of non-cytotoxic ester functionalized morpholinium based ionic liquids in aqueous media. *Journal of Colloid and Interface Science* **446**: 263–271, <https://doi.org/10.1016/j.jcis.2015.01.044>.
- Shah A, Jain M, Lad VN *et al.* (2020) Selective accumulation of dyes and curcumin in a macroscopic complex coacervates composed of morpholinium based ester functionalized ionic liquid and sodium salicylate. *Journal of Molecular Liquids* **317**: article 114140, <https://doi.org/10.1016/j.molliq.2020.114140>.
- Rajput SM, Kuddushi M, Shah A *et al.* (2020) Functionalized surfactant based catanionic vesicles as the soft template for the synthesis of hollow silica nanospheres as new age drug carrier. *Surfaces and Interfaces* **20**: article 100596, <https://doi.org/10.1016/j.surfin.2020.100596>.
- Bhadani A, Tani M, Endo T *et al.* (2015) New ester based gemini surfactants: the effect of different cationic headgroups on micellization properties and viscosity of aqueous micellar solution. *Physical Chemistry Chemical Physics* **17(29)**: 19474–19483, <https://doi.org/10.1039/c5cp02115d>.
- Kamboj R, Bharmoria P, Chauhan V *et al.* (2014) Micellization behavior of morpholinium-based amide-functionalized ionic liquids in aqueous media. *Langmuir* **30(33)**: 9920–9930, <https://doi.org/10.1021/la501897e>.
- Bhadani A, Kafle A, Koura S *et al.* (2017) Physicochemical evaluation of micellar solution and lyotropic phases formed by self-assembled aggregates of morpholinium geminis. *ACS Omega* **2(9)**: 5324–5334, <https://doi.org/10.1021/acsomega.7b00428>.
- Hwang TL, Aljuffali IA, Lin CF *et al.* (2015) Cationic additives in nanosystems activate cytotoxicity and inflammatory response of human neutrophils: lipid nanoparticles versus polymeric nanoparticles. *International Journal of Nanomedicine* **10(1)**: 371–385, <https://doi.org/10.2147/IJN.S73017>.
- Hwang TL, Sung CT, Aljuffali IA, Chang YT and Fang JY (2014) Cationic surfactants in the form of nanoparticles and micelles elicit different human neutrophil responses: a toxicological study. *Colloids and Surfaces B: Biointerfaces* **114**: 334–341, <https://doi.org/10.1016/j.colsurfb.2013.10.021>.
- Mirgorodskaya AB, Zakharova LY, Khairutdinova EI, Lukashenko SS and Sinyashin OG (2016) Supramolecular systems based on gemini surfactants for enhancing solubility of spectral probes and drugs in aqueous solution. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **510**: 33–42, <https://doi.org/10.1016/j.colsurfa.2016.07.065>.
- Mirgorodskaya AB, Valeeva FG, Zakharov SV *et al.* (2018) Aggregation behavior of morpholinium surfactants in the presence of organic electrolytes. *Russian Chemical Bulletin* **67(2)**: 291–296, <https://doi.org/10.1007/s11172-018-2072-0>.
- Kuznetsova DA, Gabdrakhmanov DR, Vasilieva EA *et al.* (2019) Supramolecular catalytic systems based on a cationic amphiphile and sodium polystyrene sulfonate for decomposition of organophosphorus pollutants. *Russian Journal of Organic Chemistry* **55(1)**: 11–16, <https://doi.org/10.1134/S1070428019010032>.
- Yackevich EI, Mirgorodskaya AB, Lukashenko SS and Zakharova LY (2014) Polyfunctional supramolecular systems based on surfactants containing the hydroxyalkyl moiety in the head group. *Russian Chemical Bulletin* **63(8)**: 1801–1806, <https://doi.org/10.1007/s11172-014-0669-5>.
- Mirgorodskaya AB, Yackevich EI, Gabdrakhmanov DR *et al.* (2016) Self-organization and lipoplex formation of cationic surfactants with morpholinium head group. *Journal of Molecular Liquids* **220**: 992–998, <https://doi.org/10.1016/j.molliq.2016.05.010>.
- Mirgorodskaya AB, Lukashenko SS, Yatskevich EI *et al.* (2014) Aggregation behavior, anticorrosion effect, and antimicrobial activity of alkylmethylmorpholinium bromides. *Protection of Metals and Physical Chemistry of Surfaces* **50(4)**: 538–542, <https://doi.org/10.1134/S207020511404011X>.
- Knaak JB, Leung HW, Stott WT, Busch J and Bilsky J (1997) Toxicology of mono-, di-, and triethanolamine. In *Reviews of Environmental Contamination and Toxicology* (Ware GW (ed.)). Springer. New York, NY, USA, pp. 1–86.

Offprint provided courtesy of www.icevirtuallibrary.com
Author copy for personal use, not for distribution

18. Fiume MM, Heldreth BA, Bergfeld WF *et al.* (2015) Safety assessment of ethanolamine and ethanolamine salts as used in cosmetics. *International Journal of Toxicology* **34**(Supplement 2): 84S–98S, <https://doi.org/10.1177/1091581815596439>.
19. Shin KO and Lee YM (2016) Simultaneous analysis of mono-, di-, and tri-ethanolamine in cosmetic products using liquid chromatography coupled tandem mass spectrometry. *Archives of Pharmacal Research* **39**(1): 66–72, <https://doi.org/10.1007/s12272-015-0677-5>.
20. Ki HM and Choi HK (2007) The effect of meloxicam/ethanolamine salt formation on percutaneous absorption of meloxicam. *Archives of Pharmacal Research* **30**(2): 215–221, <https://doi.org/10.1007/BF02977697>.
21. Lessmann H, Uter W, Schnuch A and Geier J (2009) Skin sensitizing properties of the ethanolamines mono-, di-, and triethanolamine. Data analysis of a multicentre surveillance network (IVDK) and review of the literature. *Contact Dermatitis* **60**(5): 243–255, <https://doi.org/10.1111/j.1600-0536.2009.01506.x>.
22. Lu Z, Peng X, Dorn T, Hirsch T and Stephan D (2021) Early performances of cement paste in the presence of triethanolamine: rheology, setting and microstructural development. *Journal of Applied Polymer Science* **138**(31): 1–13, <https://doi.org/10.1002/app.50753>.
23. Gwak HS, Choi JS and Choi HK (2005) Enhanced bioavailability of piroxicam via salt formation with ethanolamines. *International Journal of Pharmaceutics* **297**(1–2): 156–161, <https://doi.org/10.1016/j.ijpharm.2005.03.016>.
24. Han HK and Choi HK (2007) Improved absorption of meloxicam via salt formation with ethanolamines. *European Journal of Pharmaceutics and Biopharmaceutics* **65**(1): 99–103, <https://doi.org/10.1016/j.ejpb.2006.07.003>.
25. Rodríguez-Abreu C, Rodríguez E and Solans C (2009) Monomeric and dimeric anionic surfactants: a comparative study of self-aggregation and mineralization. *Journal of Colloid and Interface Science* **340**(2): 254–260, <https://doi.org/10.1016/j.jcis.2009.08.043>.
26. Bou Malham I, Letellier P and Turmine M (2008) Synthesis and micellar properties of 1-decyl-2,3-dimethylimidazolium bromide surfactant in water and water–ethanolamine mixtures at 298.15 K. *Journal of Colloid and Interface Science* **328**(1): 166–171, <https://doi.org/10.1016/j.jcis.2008.09.016>.
27. Carpena P, Aguiar J, Bernaola-Galván P and Carnero Ruiz C (2002) Problems associated with the treatment of conductivity–concentration data in surfactant solutions: simulations and experiments. *Langmuir* **18**(16): 6054–6058, <https://doi.org/10.1021/la025770y>.
28. Kuznetsov DM, Kuznetsova DA, Gabdrakhmanov DR *et al.* (2021) Triallyl ammonium amphiphiles: self-assembly and complexation with bovine serum albumin. *Surface Innovations*, <https://doi.org/10.1680/jsuin.21.00044>.
29. Rosen MJ (2012) Adsorption of surface-active agents at interfaces: the electrical double layer. In *Surfactants and Interfacial Phenomena*, 3rd edn. Wiley Hoboken, NJ, USA, pp. 34–104.
30. Rosen MJ (2012) Micelle formation by surfactants. In *Surfactants and Interfacial Phenomena*, 3rd edn. Wiley Hoboken, NJ, USA, pp. 105–177.
31. Zana R (1996) Critical micellization concentration of surfactants in aqueous solution and free energy of micellization. *Langmuir* **12**(5): 1208–1211, <https://doi.org/10.1021/la950691q>.
32. Rub MA, Azum N, Kumar D, Alotaibi MM and Asiri AM (2022) Impact of numerous media on association, interfacial, and thermodynamic properties of promethazine hydrochloride (PMT) + benzethonium chloride (BTC) mixture of various composition. *Journal of Molecular Liquids* **346**: article 118287, <https://doi.org/10.1016/j.molliq.2021.118287>.
33. Rub MA, Azum N, Kumar D *et al.* (2021) Aggregational behaviour of promethazine hydrochloride and TX-45 surfactant mixtures: a multi-techniques approach. *Journal of Molecular Liquids* **342**: article 117558, <https://doi.org/10.1016/j.molliq.2021.117558>.
34. Tanford C (1972) Micelle shape and size. *Journal of Physical Chemistry* **76**(21): 3020–3024, <https://doi.org/10.1021/j100665a018>.
35. Tehrani-Bagha AR, Singh RG and Holmberg K (2013) Solubilization of two organic dyes by anionic, cationic and nonionic surfactants. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **417**: 133–139, <https://doi.org/10.1016/j.colsurfa.2012.10.006>.

How can you contribute?

To discuss this paper, please submit up to 500 words to the journal office at journals@ice.org.uk. Your contribution will be forwarded to the author(s) for a reply and, if considered appropriate by the editor-in-chief, it will be published as a discussion in a future issue of the journal.

ICE Science journals rely entirely on contributions from the field of materials science and engineering. Information about how to submit your paper online is available at www.icevirtuallibrary.com/page/authors, where you will also find detailed author guidelines.