

Surface Chemical Properties and Micellization of Disodium Hexadecyl Diphenyl Ether Disulfonate in Aqueous Solution

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Abstract The surface tension of disodium hexadecyl diphenyl ether disulfonate (C₁₆-MADS) was measured at different NaCl concentrations (0.00–0.50 mol L⁻¹) and temperatures (298.0–318.0 K) using the drop-volume method. The results show that, with increasing temperature, the critical micelle concentration (CMC) of C₁₆-MADS increases slightly, but the maximum surface adsorption capacity (Γ_{\max}) at the air–water interface decreases. When the concentration of NaCl was increased from 0.00 to 0.50 mol L⁻¹, the CMC of C₁₆-MADS decreased from 1.45×10^{-4} to 4.10×10^{-5} mol L⁻¹, but the surface tension at the CMC (γ_{cmc}) was not affected. When the concentration of NaCl was increased at 298.0 and 303.0 K, the Γ_{\max} of C₁₆-MADS increased. When the temperature was increased from 308.0 to 318.0 K, the surface excess concentration (Γ_{\max}) of C₁₆-MADS abnormally decreased from 2.26 to 1.41 $\mu\text{mol m}^{-2}$ with increasing NaCl concentration. The micellization free energy ($\Delta G_{\text{m}}^{\circ}$) decreased from -63.98 to -76.20 kJ mol⁻¹ with increase of temperature and NaCl concentration. The micellar aggregation number (N_{m}) of disodium hexadecyl diphenyl ether disulfonate (C₁₆-MADS) was determined using the molecule fluorescence probe method with pyrene as probe and benzophenone as quencher. The results show that an appropriate N_{m} could be measured only at

surfactant concentration above the CMC. The N_{m} increased with an increase in C₁₆-MADS concentration, but the micropolarity in the micelle nucleus decreased. The temperature had little effect on N_{m} . Compared with typical single hydrophilic headgroup surfactants, aggregates of C₁₆-MADS exhibit different properties.

Keywords Disodium hexadecyl diphenyl ether disulfonate · Surface tension · Critical micelle concentration · Micellar aggregation number · Fluorescence probe · Micropolarity

Introduction

Disodium hexadecyl diphenyl ether disulfonate (C₁₆-MADS) is a highly efficient and multifunctional anionic surfactant with two hydrophilic headgroups. The structure of disodium hexadecyl diphenyl ether disulfonate is shown in Fig. 1. It has unique double sulfonate hydrophilic groups, which are linked by a rigid diphenyl ether group which produces intramolecular hyperconjugation. C₁₆-MADS has a variety of advantages when compared with traditional surfactants: excellent water solubility and coupling properties [1–3], extremely low Krafft point, excellent dispersion capacity [4–6], good hard water and bleach tolerance [7], and good stability in strong acid, strong alkali, and concentrated electrolyte solution [1, 8]. C₁₆-MADS has been used in high inorganic salt systems, but the effects of inorganic salt on the product have not been reported. This paper reports on the surface properties and thermodynamics of micellization of C₁₆-MADS solution using surface tension at different NaCl concentrations and temperatures. The micellar aggregation number was measured using the molecular fluorescent probe method, and

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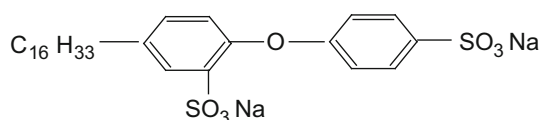


Fig. 1 Structure of disodium hexadecyl diphenyl ether disulfonate

changes of concentration, temperature, inorganic salt effect, and micropolarity were investigated. The results show that C_{16} -MADS exhibits obvious differences compared with traditional surfactants [9–11].

Experimental

Materials

NaCl (AR, Shanghai Chemical Reagent Co., Ltd., used after calcining at 500 °C for 5 h), C_{16} -MADS [homemade, high-performance liquid chromatography (HPLC) and mass spectrometry assay, content 99.8 %] [12], ultrapure water (Wuxi New Central Asia Institute of Microelectronics, conductivity 7.8×10^{-7} S cm^{-1}), anhydrous methanol, ethanol, petroleum ether, pyrene (Sigma-Aldrich, 99.0 %), and benzophenone (CP, Shanghai Qunli Chemical Co., Ltd.) were used.

Measurements of Surface Tension

Solutions of C_{16} -MADS were prepared at different concentrations using ultrapure water. The surface tension was measured with a DCA-315 automatic interfacial tensiometer (Thermo Cahn Co., USA) by pendant drop method at 298.0 ± 0.1 , 303.0 ± 0.1 , 308.0 ± 0.1 , 313.0 ± 0.1 , and 318.0 ± 0.1 K.

Measurement of Micellar Aggregation Number

The micellar aggregation number of C_{16} -MADS was determined using the molecule fluorescence probe method with pyrene (Py) as probe (P) and benzophenone (DPK) as quencher (Q), with an RF-5301PC spectrofluorophotometer (Shimadzu Scientific Instruments). The fine structure of the steady-state fluorescence spectrum of pyrene has five vibronic peaks at wavelengths of 373, 379, 384, 390, and 393 nm [13]. In aqueous solution, pyrene and benzophenone can be closely integrated within surfactant micelles, and residence time in micelles is much longer than the probe's fluorescence lifetime. If (1) the quenching of Q for P is static quenching, (2) the kinetic coefficient $R = (K_f + K_D)/K_q \approx 0$ (where K_f , K_D , and K_q are constants of stimulated emission fluorescence, nonradiative decay, and quenching, respectively), and (3) Q follows the

Poisson distribution between micelles, the following formula can be deduced [14]:

$$\ln I_1 = -N_m \times C_Q / (S_T - \text{cmc}) + \ln I_0, \quad (1)$$

where I_1 is the fluorescence intensity when the concentration of quencher is [Q] and the wavelength is 373 nm, I_0 is the fluorescence intensity without the quencher, C_Q is the concentration of the quencher, S_T is the total concentration of surfactant, and cmc is the critical micelle concentration of the surfactant. Equation (1) can be converted to read

$$\ln(I_0/I_1) = N_m \times C_Q / (S_T - \text{cmc}), \quad (2)$$

$$[\ln(I_0/I_1)]^{-1} = (N_m \times C_Q)^{-1} (S_T - \text{cmc}). \quad (3)$$

As can be seen from the above equations, when C_Q is fixed, N_m can be deduced from the relationship between $[\ln(I_0/I_1)]^{-1}$ and S_T .

Measurement Methods for Micellar Aggregation Number

Solutions of C_{16} -MADS at different concentrations were prepared using water saturated with pyrene as solvent. Benzophenone of a certain concentration was prepared using anhydrous methanol as solvent. A certain amount of methanol solution of benzophenone was accurately weighed into a clean, dry 100-mL flask with stopper, and the methanol was dried under pure nitrogen. The solutions of prepared surfactant and pyrene were accurately transferred to flask with a pipette. After agitation in an ultrasonic bath for 10 min, solutions were equilibrated in a constant-temperature water bath for 12 h. Binary solutions of the same probe and surfactant concentration but without quencher were prepared as reference reagent. The fluorescence intensity of the solutions was measured by fluorescence spectrometer with excitation wavelength of 335 nm. I_1 and I_0 were measured at 373 nm using slit width of 1.5 nm.

Results and Discussion

Effect of NaCl Concentration on Surface Tension

The surface tension of C_{16} -MADS solutions at different concentrations was measured for different NaCl concentrations (0.00, 0.05, 0.10, 0.20, and 0.50 mol L^{-1}) and temperatures (298.0, 303.0, 308.0, 313.0, and 318.0 K). The surface tension isotherms are shown in Fig. 2.

The critical micelle concentration (CMC) and the surface tension at the critical micelle concentration (γ_{cmc}) are important parameters to assess the surface activity of surfactants [15]. For conventional ionic surfactants, when

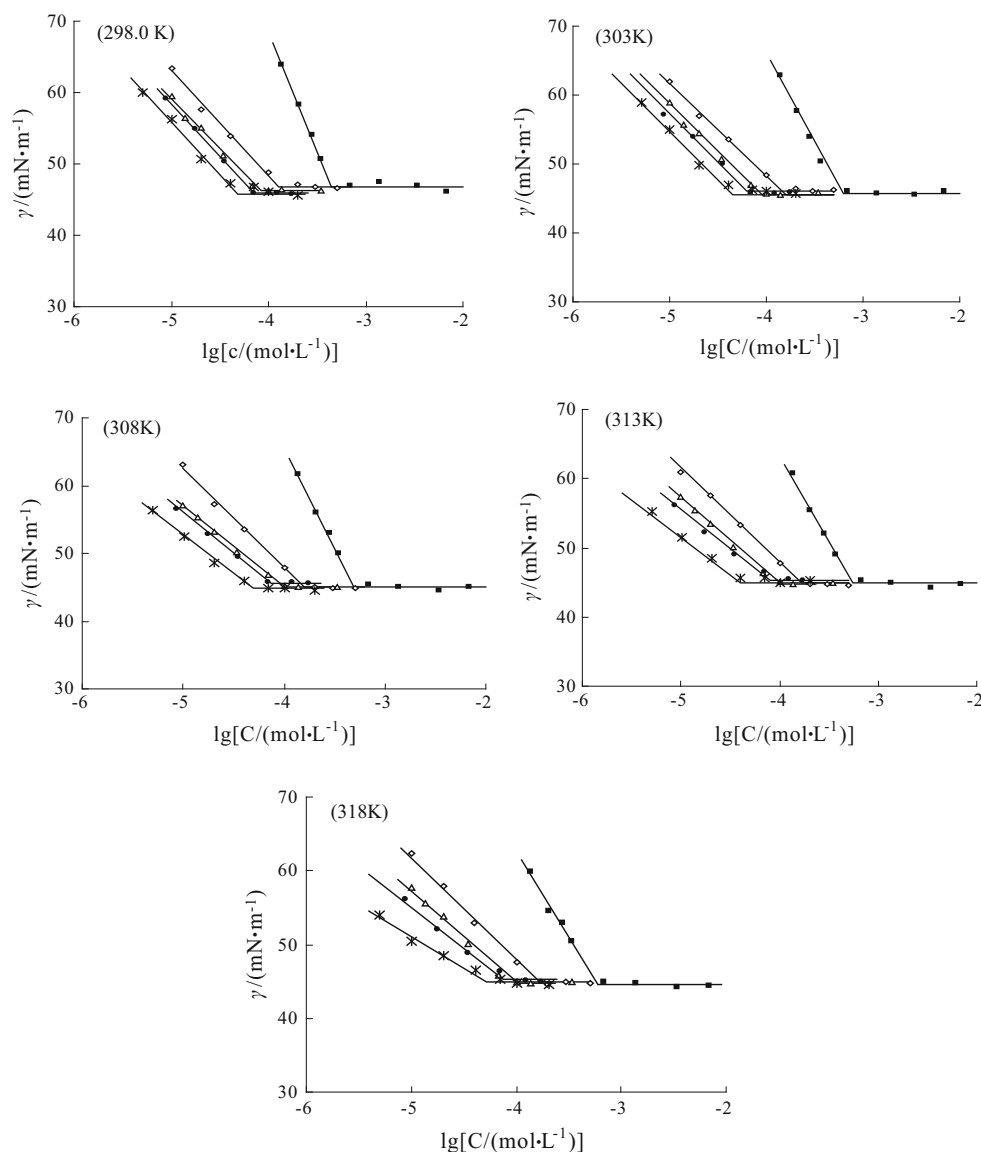


Fig. 2 Effect of NaCl concentration on surface tension of C₁₆-MADS in aqueous solution at different temperatures. c_{NaCl} (mol L⁻¹): square 0.00, diamond 0.05, triangle 0.10, circle 0.20, asterisk 0.50

the inorganic salt added is the same as the surfactant counterion, the surface activity is improved while the CMC and γ_{cmc} decrease. This is mainly because the hydration film is damaged with addition of inorganic salt and the diffuse double layer is compressed around the ionic headgroups. When the electrostatic repulsion is shielded, and surfactant molecules in the surface layer of the micelle can arrange more closely, micelles can form more easily [16]. The CMC of C₁₆-MADS solution significantly decreased with addition of NaCl, but γ_{cmc} remained essentially unchanged because the two hydrophilic groups are linked with a rigid diphenyl ether group which lacks flexibility.

Surface Chemical Properties of Disodium Hexadecyl Diphenyl Ether Disulfonate

According to the Gibbs adsorption equation, under excess counterion conditions, the change in surface tension (γ) is given by [16, 17]

$$-d\gamma = \Gamma_s RT d \ln C_s, \quad (4)$$

where Γ_s is the surface adsorption of the surfactant, R is the gas constant, T is the temperature in Kelvin, and C_s is the concentration of surfactant ions in solution. Then, the maximum adsorption (Γ_{max}) of the solution surface can be calculated from Eq. (5).

$$\Gamma_{\max} = -d\gamma/(RTd \ln C_s) = -d\gamma/(2.303RTd \log C_s). \quad (5)$$

Γ_{\max} can be obtained from the slope of γ versus $\log C_s$ curves [15, 18]. The average minimum area per molecule in a monolayer (A_{\min}) can be calculated from Eq. (6):

$$A_{\min} = 1/N_A \cdot \Gamma_{\max}, \quad (6)$$

where N_A is Avogadro's constant. Table 1 shows that the CMC of C₁₆-MADS increased gradually with increasing temperature at all NaCl concentrations. The hydration of the hydrophilic headgroup decreases with increasing temperature, so micelle formation is easier. On the other hand, the structure of water around the hydrophobic tail group is disrupted with increasing temperature, which is not conducive to micelle formation. Normally, the effect of temperature on the hydrophobic effect plays the dominant role, so the CMC of C₁₆-MADS solution tends to increase with increasing temperature. Likewise, the Γ_{\max} value of the C₁₆-MADS solution decreased slightly with increasing temperature at given NaCl concentration, and the average molecular area increased.

Increase in the NaCl concentration affects two aspects of C₁₆-MADS at 298.0 and 303.0 K. On the one hand, the ionic strength of the solution is changed, so the activity of the surface-active ion is changed. Surface adsorption as a balance property must also change with the change in activity. On the other hand, it is conducive to the combination of the counterion and the surface-active ions due to the increase in counterion concentration, which weakens the electrical repulsion in the adsorption layer, so the adsorbed molecules can pack more closely, thus Γ_{\max} increases.

The Γ_{\max} value of C₁₆-MADS decreased with increase of the NaCl concentration at 308.0, 313.0, and 318.0 K. This occurs not only because the molecular thermal motion is strengthened and the tendency for protonation of C₁₆-MADS ions is weakened, but because the combined action of temperature and NaCl is also a major factor. According to Bjerrum theory [19], when the NaCl concentration and temperature increase, ion hydration is weakened in solution. The distance between the positive and negative ions is

Table 1 Surface chemical properties of C₁₆-MADS in aqueous solution

c_{NaCl} (mol L ⁻¹)	T (K)	cmc (mmol L ⁻¹)	γ_{cmc} (mN m ⁻¹)	Γ_{\max} ($\mu\text{mol m}^{-2}$)	A_{\min} (nm ²)	cmc/ C_{20} ^a	pC ₂₀
0.00	298.0	0.451	46.7	2.21	0.75	1.430	3.500
	303.0	0.470	46.3	2.21	0.75	1.542	3.516
	308.0	0.498	45.5	2.18	0.76	1.720	3.542
	313.0	0.542	45.4	2.18	0.76	1.893	3.553
	318.0	0.604	45.4	2.18	0.76	2.115	3.571
0.05	298.0	0.145	46.8	2.27	0.73	2.255	4.192
	303.0	0.150	46.5	2.27	0.73	2.489	4.220
	308.0	0.158	45.0	2.27	0.73	3.021	4.281
	313.0	0.161	45.0	2.24	0.74	3.132	4.289
	318.0	0.166	45.0	2.24	0.74	3.262	4.293
0.10	298.0	0.089	46.3	2.27	0.73	2.566	4.460
	303.0	0.094	45.8	2.27	0.73	2.742	4.465
	308.0	0.100	45.1	2.16	0.77	3.002	4.477
	313.0	0.103	44.9	2.12	0.78	3.176	4.489
	318.0	0.105	44.8	2.10	0.79	3.297	4.497
0.20	298.0	0.062	45.9	2.55	0.66	2.617	4.625
	303.0	0.065	45.8	2.31	0.72	2.890	4.648
	308.0	0.069	45.5	2.08	0.80	3.391	4.691
	313.0	0.073	45.3	1.94	0.86	3.684	4.703
	318.0	0.076	45.2	1.83	0.91	4.061	4.728
0.50	298.0	0.041	45.8	2.58	0.64	2.637	4.808
	303.0	0.044	45.4	2.37	0.70	3.247	4.868
	308.0	0.048	44.8	1.94	0.86	4.250	4.947
	313.0	0.050	45.0	1.60	1.04	5.272	5.023
	318.0	0.053	45.0	1.41	1.12	6.557	5.092

The cmc/ C_{20} ratio measures the tendency of the surfactant to adsorb at the interface relative to its micellization tendency

^a C_{20} is the surfactant molar concentration required to reduce the surface tension of water by 20 mN m⁻¹. pC₂₀ = -lg C_{20}

shortened, and the electronegativity of Cl⁻ is greater than that of the C₁₆-MADS ionic headgroup. When the electrostatic attraction energy between Na⁺ and Cl⁻ is larger than the thermal motion energy, a relatively stable ion pair, reducing the number of counterions in the C₁₆-MADS ionic headgroup, increasing the electronegativity and electrical repulsion of the C₁₆-MADS ionic headgroup above that of traditional anionic surfactants, so Γ_{max} decreases. This is also consistent with decreasing detergency with increase of temperature [20].

Thermodynamic Parameters of Micellization

For 2–1-type ionic surfactants with an excess of inorganic salt, the free energy of micellization (ΔG_m^o), enthalpy (ΔH_m^o), and entropy (ΔS_m^o) can be calculated by the thermodynamic functions [15, 16]

$$\Delta G_m^o = 3RT \ln \text{cmc} + 2RT \ln 2, \tag{7}$$

$$\Delta H_m^o = -3RT^2 \left(\frac{\partial \ln \text{cmc}}{\partial T} \right)_p, \tag{8}$$

$$\Delta S_m^o = \frac{1}{T} (\Delta H_m^o - \Delta G_m^o). \tag{9}$$

The micellization thermodynamics of C₁₆-MADS are given in Table 2. ΔG_m^o is negative at all temperatures, which suggests that micellization can occur spontaneously.

ΔH_m^o is the micelle formation heat, which is an important thermodynamic parameter for the micelle formation process [21, 22]. ΔH_m^o < 0 suggests that micelle formation is an exothermic process, because the C₁₆-MADS molecule loses translational energy when micelles form, and the heat released from the interaction of the hydrocarbon chains exceeds that from the “iceberg structure.” The decrease of ΔH_m^o indicates that C₁₆-MADS molecules have a stronger tendency to form micelles spontaneously in solution [23]. The ΔH_m^o of C₁₆-MADS solution is small when C_{NaCl} = 0.50 mol L⁻¹, so its CMC is small. The entropy (ΔS_m^o) reflects the changes of disorder in the process of transition state formation. All the ΔS_m^o values are positive, which means that it is easy to carry out the process in which C₁₆-MADS molecules are added to the micelles. In aqueous solution, water molecules around C₁₆-MADS molecules can form an ordered region, which is called the “iceberg structure.” After micelles are formed, the “iceberg structure” around the molecules disintegrates, and the disorder of the system is increased, so the ΔS_m^o value becomes positive. It can also be seen from Table 2 that ΔS_m^o decreases with increasing temperature. This is because the micellization tendency of C₁₆-MADS weakens when the temperature increases. Meanwhile, the absolute value of ΔH_m^o is smaller than the absolute value of -TΔS_m^o, so the formation process of C₁₆-MADS micelles is a mainly entropy-driven process.

Table 2 Thermodynamic parameters of micellization of C₁₆-MADS

c _{NaCl} (mol L ⁻¹)	T (K)	ΔG _m ^o (kJ mol ⁻¹)	ΔH _m ^o (kJ mol ⁻¹)	ΔS _m ^o (kJ mol ⁻¹ K ⁻¹)	TΔS _m ^o (kJ mol ⁻¹)
0.05	298.0	-63.98	-14.95	0.1645	-49.03
	303.0	-64.79	-15.46	0.1628	-49.33
	308.0	-65.47	-15.97	0.1607	-49.50
	313.0	-66.39	-16.75	0.1586	-49.64
	318.0	-67.20	-17.43	0.1565	-49.77
0.10	298.0	-67.60	-18.27	0.1655	-49.33
	303.0	-68.32	-18.89	0.1631	-49.43
	308.0	-68.99	-19.38	0.1610	-49.61
	313.0	-69.87	-20.11	0.1590	-49.76
	318.0	-70.14	-20.31	0.1567	-49.83
0.20	298.0	-70.30	-20.82	0.1660	-49.48
	303.0	-71.11	-21.53	0.1636	-49.58
	308.0	-71.83	-22.14	0.1613	-49.69
	313.0	-72.56	-22.76	0.1592	-49.80
	318.0	-73.30	-23.21	0.1575	-50.10
0.50	298.0	-73.40	-23.81	0.1664	-49.59
	303.0	-74.06	-24.36	0.1640	-49.70
	308.0	-74.60	-24.74	0.1619	-49.86
	313.0	-75.52	-25.55	0.1596	-49.97
	318.0	-76.20	-25.91	0.1581	-50.29

Table 3 N_m of C_{16} -MADS at different concentrations and temperatures

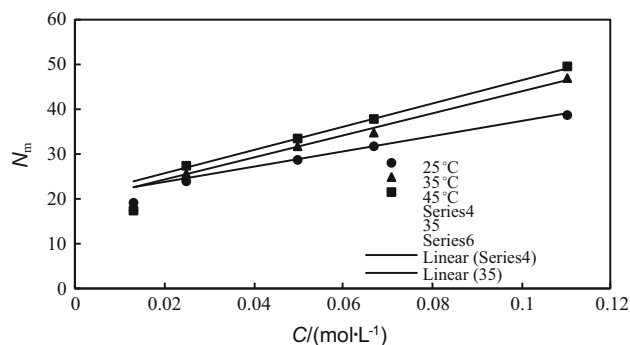
Surfactant concentration (mol L ⁻¹)	N_m		
	25 °C	35 °C	45 °C
1.32×10^{-2}	19	18	18
2.48×10^{-2}	25	26	28
5.00×10^{-2}	30	32	32
6.68×10^{-2}	34	35	35
1.10×10^{-1}	39	47	49
4.0×10^{-2} (SDS) [10]	60		

Measurements of Micellar Aggregation Number

Solutions of C_{16} -MADS at different concentrations were prepared using pyrene-saturated water solution as solvent with quencher concentration of 1.0 mmol L⁻¹, and the micellar aggregation number (N_m) was determined by the molecular fluorescent probe method. The results are shown in Table 3.

For traditional surfactants, the appropriate N_m of spherical micelles can be measured when the surfactant concentration is within 10 times of the CMC. For C_{16} -MADS, the measured N_m was very small when the concentration was low. There are two kinds of forces that control surfactant aggregation. One is the hydrophobic interaction between alkane chains, which is the force that drives surfactant molecules to spontaneously form orderly aggregates. The other is the repulsive force between ion headgroups, which is caused by electrostatic repulsion or hydration layer resistance. For C_{16} -MADS, the force of the latter is larger than that of the former, and the two hydrophilic groups linked by a rigid group have no bending flexibility. The cross-sectional area of each molecule is large, which hinders the formation of close aggregation. So C_{16} -MADS tends to be adsorbed at the interface (surface) when the concentration is low, and the tendency to form micelles is relatively weak. The arrangement of surfactant molecules which contribute to micelle formation is loose, so it cannot solubilize enough probe and quencher. This is also the main reason why C_{16} -MADS behaves differently from conventional surfactants. It is also different from other gemini surfactants, which exhibit a strong tendency for micellization in aqueous solution [24]. For this reason, N_m had to be measured at a higher concentration range.

The micellar aggregation number (N_m) measured at different temperatures versus concentration is shown in Fig. 3. The micellar aggregation number increases with increasing concentration. N_m is not sensitive to temperature variations when the surfactant concentration is from 1.32×10^{-2} to 6.68×10^{-2} mol L⁻¹, which shows that

**Fig. 3** Relationship between N_m and C of C_{16} -MADS**Table 4** Critical micellar aggregation number

Surfactant	N_m		
C_{16} -MADS	21 (25 °C)	20 (35 °C)	21 (45 °C)
SDS [25]	57 (25 °C)	49 (40 °C)	

temperature has little influence on the surfactant. However, N_m changes significantly with temperature when the concentration reaches 1.10×10^{-1} mol L⁻¹. This is probably due to a sphere to rod transition.

Critical Micellar Aggregation Number

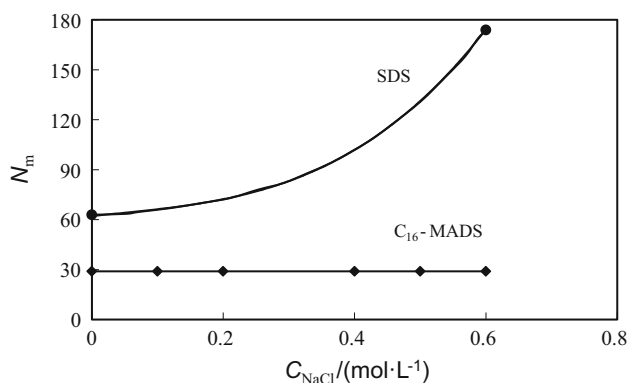
In this work, the critical micellar aggregation number [N_m] of C_{16} -MADS was obtained by extrapolating the aggregation number to the CMC. As shown in Table 4, the [N_m] of C_{16} -MADS is much lower than that of sodium dodecyl sulfate (SDS). This also shows that the force between headgroups of the double hydrophilic group surfactant is strong. The micellization tendency is relatively weak when the solution concentration is low. At the same time, the effect of temperature on the [N_m] of C_{16} -MADS is also less than the effect on the [N_m] of SDS. So, the C_{16} -MADS solution is stable at low concentration (Table 5).

Relationship Between Micellar Aggregation Number and NaCl Concentration

For traditional ionic surfactants with a single hydrophilic group, there is an electrical double layer around the micelle with a hydration film formed by water molecules. The hydration film is destroyed with addition of NaCl, and the diffuse double layer around the ionic groups is compressed, which increases N_m significantly. Chen Jingyuan [26–28] showed that the N_m of SDS increases sharply from 63 to 176 when the concentration of NaCl is 0.6 mol L⁻¹. Figure 4 shows that the N_m value of C_{16} -MADS is not significantly affected by addition of NaCl. The double

Table 5 Values of I_1/I_3 of C_{16} -MADS at different concentrations and temperatures

Surfactant concentration (mol L ⁻¹)	I_1/I_3		
	25 °C	35 °C	45 °C
1.32×10^{-2}	1.21	1.12	1.20
2.48×10^{-2}	1.15	1.16	1.14
5.00×10^{-2}	1.10	1.11	1.10
6.68×10^{-2}	1.09	1.07	1.06
1.10×10^{-1}	1.05	1.04	1.04
1.04×10^{-2} (SDS) [26]	0.98		

**Fig. 4** Dependence of N_m of 3.80×10^{-2} mol L⁻¹ C_{16} -MADS solution on NaCl concentration at 25 °C

hydrophilic group of C_{16} -MADS and the hyperconjugation make the interaction between molecular electric charges larger, and steric effects also prevent molecules outside the micelles from entering. So NaCl has little effect on the N_m , which illustrates that C_{16} -MADS has excellent salt resistance properties. This is a significant feature of the surfactant, which also explains why it can be applied in special areas.

Changes of I_1/I_3

I_1 and I_3 were obtained from the pyrene fluorescence spectra. The micropolarity of micelle nucleus around the pyrene probe can be reflected by the ratio of I_1 and I_3 [29, 30]. Pyrene should be solubilized in the palisade layers near the surfactant polar head. Increase of the concentration of C_{16} -MADS and the micellar aggregation number is likely to cause the surfactant molecules to pack more closely, which excludes water from the palisade layer. Meanwhile, pyrene molecules can transfer to the micelle interior, making its microenvironment less polar, so the value of I_1/I_3 decreases with increasing concentration. Temperature has almost no influence on the I_1/I_3 ratio of

C_{16} -MADS. The micropolarity of micelle nucleus of C_{16} -MADS is stronger than SDS, which shows that the polarity of the former is greater than that of the latter, and this also agrees with the molecular structure of C_{16} -MADS.

Conclusions

For certain NaCl concentrations, the CMC of C_{16} -MADS solution increases slightly with increasing temperature, while Γ_{max} decreases. The CMC decreases significantly with increasing NaCl concentration while γ_{cmc} remains essentially unaffected. At 298.0 and 303.0 K, the Γ_{max} of C_{16} -MADS solution increases with increasing NaCl concentration. When the temperature is 308.0, 313.0, and 318.0 K, the Γ_{max} of C_{16} -MADS solution shows a surprising decrease with increasing NaCl concentration. The thermodynamic parameters of micellization of C_{16} -MADS have been calculated, showing that the process of micellization of C_{16} -MADS is a spontaneous entropy-driven process.

C_{16} -MADS has a strong tendency to adsorb at the air-water interface, and the tendency for forming micelles is relatively weak. The micellar aggregation number is about half those of traditional anionic surfactants, while the micropolarity of the micellar nucleus is larger. Inorganic salt has little effect on N_m . When the surfactant concentration is in the range from 1.32×10^{-2} to 1.10×10^{-1} mol L⁻¹, the micellar aggregation number increases linearly with increasing concentration, and the micropolarity of micelle nucleus decreases. In addition, temperature has little effect on N_m in this range.

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